THE EFFECT OF CERTAIN ADDITIVES UPON THE PHYSICAL PROPERTIES OF PORTLAND CEMENT

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THE PHYSICAL PROPERTIES OF PORTLAND CEMENT

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To Miss Elizabeth Atwood, for her kind, loyal assistance with so many phases of the work, I lovingly dedicate this thesis.

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CHAPTER I

INTRODUCTION

The petroleum industry is constantly engaged in the search for new oil reserves, particularly in the areas where producing fields are already established. Thus the trend in the past few decades has been toward wells of increasing depth. In these deeper wells, as in previous years, it is common practice to cement in the casing.* This operation involves the pumping of neat cement slurries into the annular space between the earth's formation and the casing to provide stability for the underground pipe and to create a permanent seal. This eliminates the possibility of contamination of surface or artesian water, by salt water from the well, and prevents any water from water-bearing strata from entering the well. A diagram of a typical well cementing job is shown on Figure I.

The depth to which oil and gas wells have been drilled in this country has been continually increasing since the

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*State law in California requires a pressure test on all cementing jobs, and all wells to be abandoned must be filled with cement.

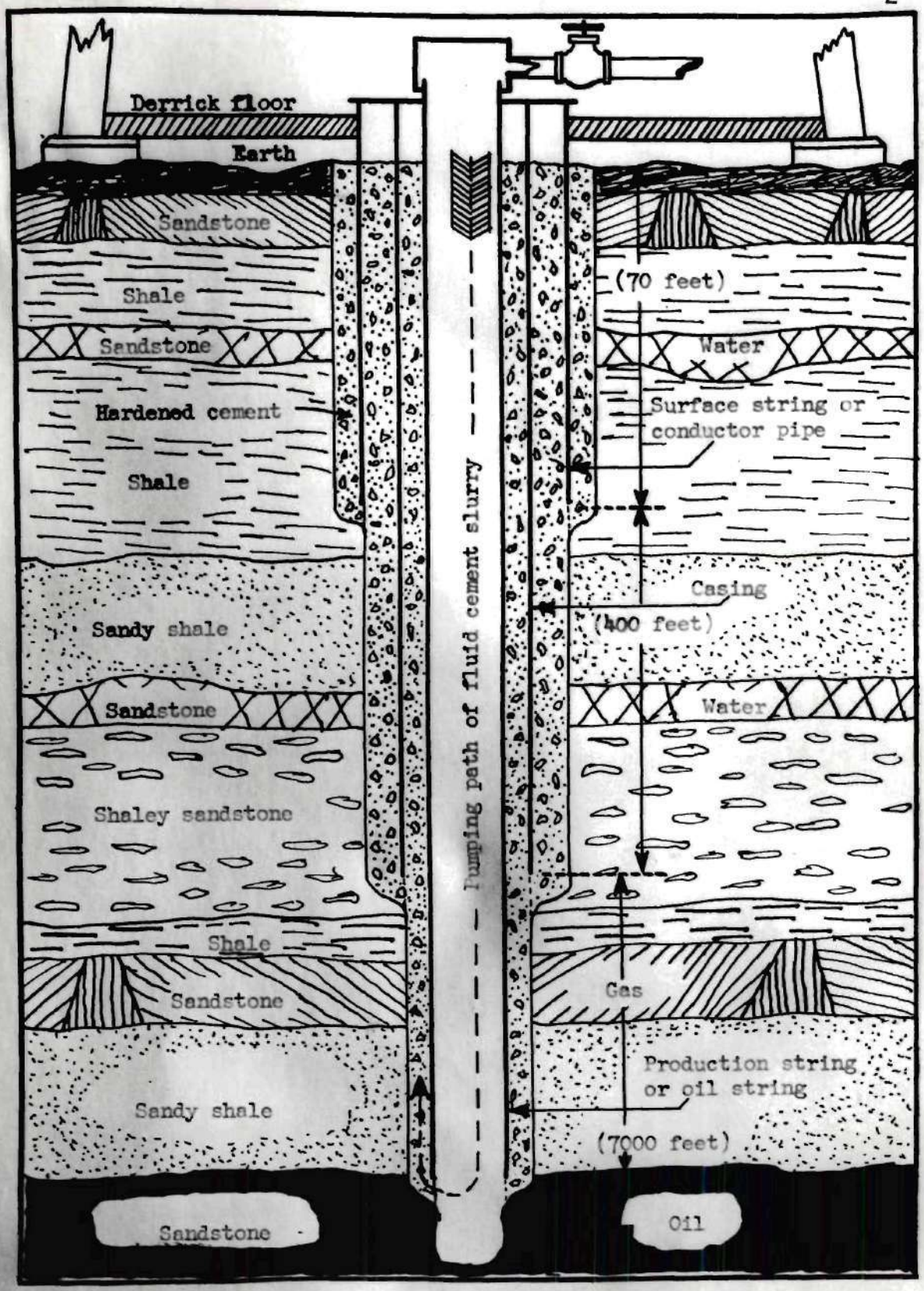

FIGURE 1

CROSS-SECTION OF OIL WELL WITH CEMENTED CASING

days of Drake's well, the first commercial producer in this country, completed in 1859. Whereas "Colonel" Drake sank this well only 69½ feet, at Watsons Flat, Pennsylvania, the latest sources[1] show that in June, 1949 a test hole was drilled to a depth of 20,521 feet, making it the world's deepest well at the present time. Figure 2 shows the relationship between the deepest wells drilled and the years in which they were completed.

Depletion of shallow reserves has necessitated exploration of and production from continually increasing depths. Accompanying this increase in depth were many serious problems caused by the temperatures and pressures encountered in the earth. There is a geothermal gradient which is rather uniform in any given area, of about 1°F for every 50 feet of depth. Although the surface temperature changes with the seasons, this gradient remains nearly unchanged. A typical geothermal gradient condition is shown on Figure 3.

The normal formation pressure encountered is equal to the hydrostatic head of water from the surface down to the formation, although, occasionally, abnormally high pressures are found which usually are due either to hills in the vicinity or to the transmission of part of the weight of the overburden as pressure to the formation fluids.

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[1] Esso Oilway 16, No. 10, 1,(1950).

Figure 2

Yearly Increase of Oil Well Depths

The data used in this plot were from Esso Oilway 16, No. 10, 1, (1950); Petroleum Facts and Figures, Am. Petroleum Inst. 6th Edition, 68, (1939); and Petroleum Facts and Figures, Am. Petroleum Inst. 8th Edition, 89, (1947).

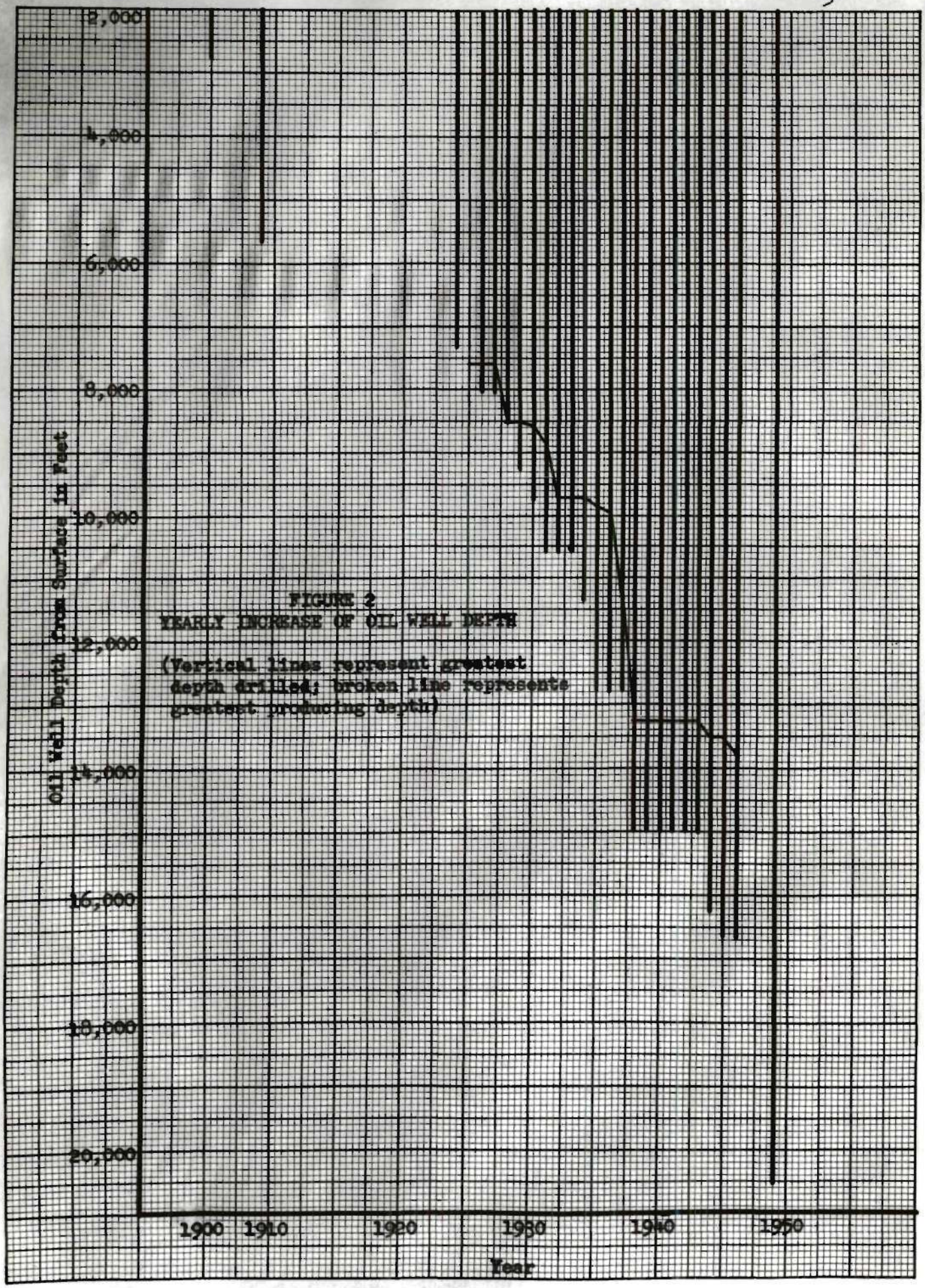

FIGURE 2
YEARLY INCREASE OF OIL WELL DEPTH

(Vertical lines represent greatest depth drilled; broken line represents greatest producing depth)

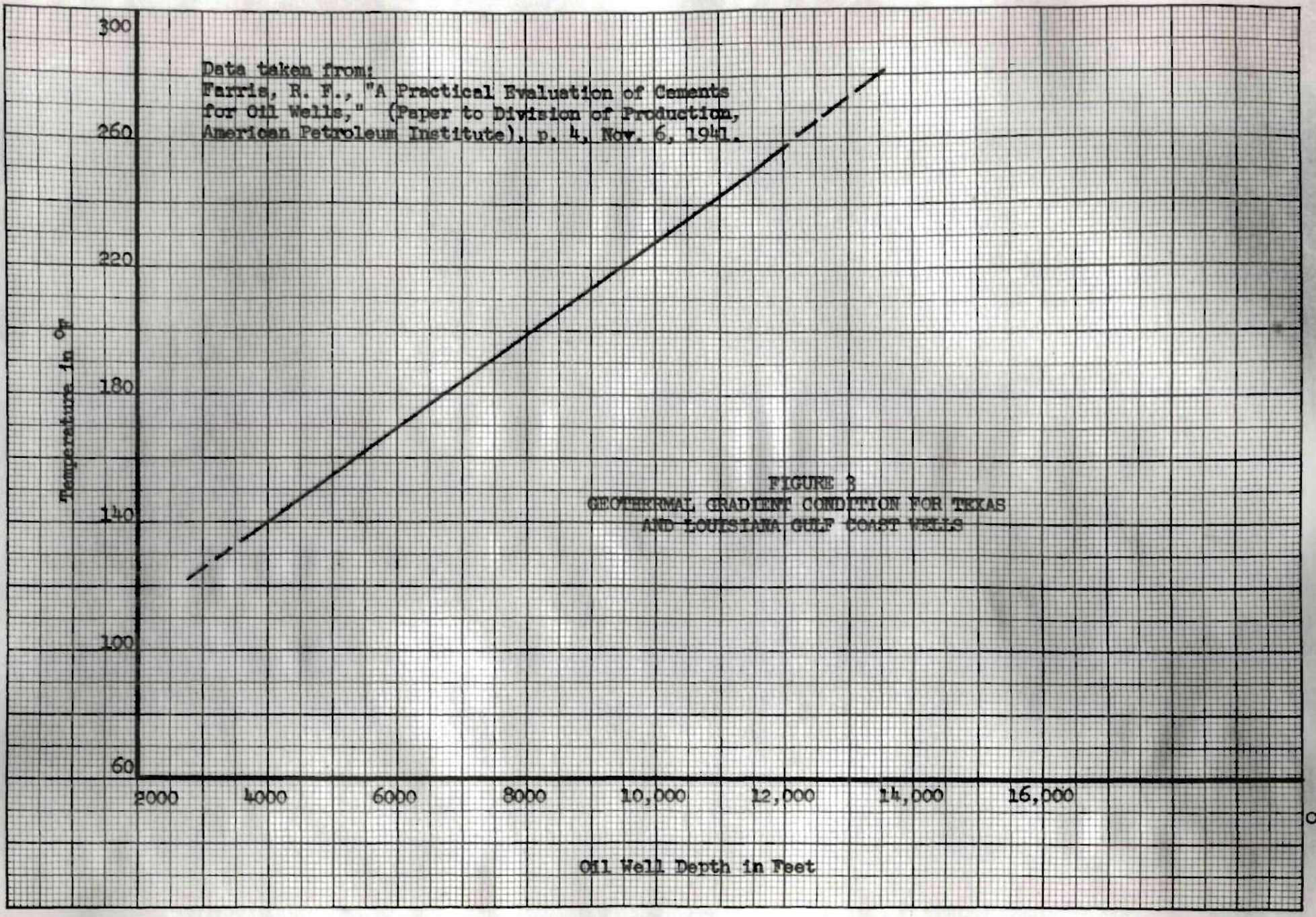

FIGURE 3
GEOTHERMAL GRADIENT CONDITION FOR TEXAS AND LOUISIANA GULF COAST WELLS

These conditions have important effects upon the setting rate of cement. That is, an increase in either temperature or pressure will increase the setting rate, thereby shortening the allowable cementing time. Since the cement slurry is pumped into the well as a "viscous fluid," this allowable cementing time is that period during which it is thin enough to be pumped. The terms, limit of pumpability and limit of mobility, have been used in industry to denote the condition of the cement slurry at the end of the allowable cementing time.

It may be realized that the deeper the cement goes into a well, the greater is the setting rate, due to higher temperature and pressure. Yet, the greater is the amount of time required to pump a unit quantity of cement to the bottom of the well, and into place. Consequently, a cement had to be developed which would meet the conditions in deep wells and still remain mobile.

In the past this has been a "tailor-made" cement with a base of Portland-type cement, but one which had been prepared according to a special formula requiring chemical additives or special mill treatment and compounding. Consequently, it has sold for a premium price, although the amount of special chemical ingredients seldom equalled one per cent of the total weight of the mixture. As an example, during 1944, at the peak of wartime production, the average

national price for oil-well cement was $1.94/bbl., but the standard Portland cement sold for $1.56/bbl.[2]

These special cements, being ready-made, were designed for a wide range of applicability in order to try to meet the various conditions that might be expected in the field. Naturally there could be little specificity, since the manufacturer tried to produce a composition that would strike a happy medium between cost and performance.

From the standpoint of the majority of cementing requirements, a 40 per cent cement slurry should reveal certain characteristics, and these have been variously defined. Ludwig[3] said:

> "A cement for use in oil wells should have the following properties:
>
> (1) The cement slurry should remain fluid for a period of several hours at temperatures of 140° to 200°F and then stiffen and harden rapidly.
>
> (2) The cement slurry should remain pumpable during the first few hours even when allowed to stand at rest for short periods of time."

The manufacturers of the Halliburton Consistometer are even more specific. Their instruction pamphlet states that the following characteristics should be revealed on a consistency-time curve produced with a 40 per cent slurry at 180°F in the Halliburton Consistometer.

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[2] U. S. Minerals Yearbook for 1944, 1230, Washington, D. C. (1946).

[3] Ludwig, N. C., Oil Gas J. 46, No. 14, 105, (1947).

(1) Initial consistency between 10 and 30 poises.

(2) Consistency to remain below 40 poises for three hours from the time of introduction into the consistometer.

(3) A sharp break toward higher consistency after three hours.

(4) A tangent to the consistency-time curve should be practically vertical when the curve reaches a consistency of 100 poises. This feature is indicative of the rapidity with which the cement will develop strength after the initial set.

The object of this investigation was (1) to make a literature study and evaluation of additives and treatments used for oil-well cements and (2) to conduct an experimental program in search of some substance that would act more effectively as a set-retarding agent when added to ordinary, gray, Type I Portland cement. This agent should not affect or should even increase the strength of the cement after 24 hours. This is important, because the cement should have a high early-strength in order to allow continuation of drilling operations in the well within a maximum of one or two days. If such an agent could be added during field operations, it would have two definite advantages: (1) it would eliminate the purchase of commercial oil-well cement at a premium price and (2) it would allow the operator a manual control over the quantity of additive, consequently better control of setting rate to give a better cementing job.

One of the more important properties of any oil-well cement isthe compressive strength it develops when hardened.

Practically all chemical additives that have been used in the past have lowered the strength of the hardened cement, so it would be of a distinct advantage to the cementing industry to find some additive which would retard the set without sacrificing any of the resultant compressive strength.

Realizing this, any investigation would be incomplete without compression tests on the hardened cement from the test slurries. Therefore, the ultimate compressive strength was measured, as well as the limit of mobility, in this investigation.

CHAPTER II

THEORY OF SETTING AND HARDENING

Portland cement is a finely-ground mixture of calcium aluminates and silicates capable of setting and hardening by chemical reaction with water. Basically, it is made by fusing together two materials, one calcareous or rich in lime, such as limestone, marl or chalk, and the other argillaceous, or rich in silica and alumina, such as clay, shale, slate or blast-furnace slag. More specifically, it has been defined in the Standards of the American Society for Testing Materials[4] as:

> "The product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates, to which no additions have been made subsequent to calcination other than water and/or untreated calcium sulfate, except that additions not to exceed 1.0 per cent of other materials may be interground with the clinker at the option of the manufacturer, provided such materials in the amount indicated have been shown to be not harmful by tests carried out or reviewed by Committee C-1 on cement."

Five types of Portland cement are recognized in the United States but the only one used in these tests was Type I, or ordinary gray Portland cement. It is specified as:[5]

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[4] Am. Soc. Testing Materials, Standards. Part II, 1, (1946)

[5] Am. Soc. Testing Materials, Standards. Part II, 1,(1944)

> "Normal Fineness, Type I, For use in general concrete construction where the special properties specified for types II, III, IV and V are not required."

A standard specification is also set up for the chemical composition of the cement and Table I shows the specifications for Type I, in maximum percentages of ingredients, followed by the actual analysis of a typical Type I cement.

TABLE I[6]

SPECIFIED CHEMICAL REQUIREMENTS AND TYPICAL ANALYSIS FOR TYPE I PORTLAND CEMENT

	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	Ign. Loss %	Insol. Resid. %
Max.	-	-	-	-	5.0	2.0	3.0	0.75
Typ.	21.3	6.0	2.7	63.2	2.9	1.8	1.3	0.20

Reactions between water and the compounds present in Portland cement lead to the setting and hardening of the material and the interactions of the cement compounds with water may be considered as of two kinds, hydrolysis and hydration. In practice both types of reactions occur simultaneously, but for the purpose of a better understanding

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[6] Research Reports, Portland Cement Association of the United States of America, 3, April, 1941.

it is important to distinguish between them and to treat them separately.

The terms, initial set and final set, are expressions which have been given arbitrary values[7] that are a measure of the progress of such reactions, but the term, setting, has reference to the change from a fluid to a rigid state.

Since the initial set indicates the time when the cement is no longer fluid to any appreciable extent, the limit of mobility of a neat* cement slurry will be reached sometime before the initial set. Setting may be distinguished from hardening by the difference in speed of the hydration reactions. During hardening water diffuses slowly through s sheath of gel to the unaltered grains below. The rate of chemical reaction, which is determined by the rate of diffusion, is very slow.

However, during the early period of setting, the mixing water is in immediate contact with the reactive surfaces of the cement grains. Solution, hydration and hydrolysis may then take place with relative rapidity. As the mixing water leaves the free condition to become fixed as

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[7] Am. Soc. Testing Materials, Standards. Part II, 25, (1944).

*Neat cement refers to a mixture of any Portland cement and water, to which no aggregate, such as sand or gravel, has been added. All slurries tested in this investigation were of neat cement.

hydrate, the plastic mass stiffens and sets. If the rate of hydration is slow, the set will be slow; conversely, if the rate of hydration is rapid, the plastic mass will set rapidly.

Neighbors and Cromer[8] said:

> "The more rapid rate of stiffening is probably due to the accelerated rate of hydration produced by heat. --- There seems to be no practical and positive method for obtaining information on the rate at which cement becomes heated while being pumped into a well. Evidently it begins to take on heat by conduction through the casing from the (drilling) mud returns. The temperature probably continues to rise and possibly does not attain a maximum value until the slurry is in place. --- Many authorities believe that on the ordinary cementing job slurry temperatures during placement do not exceed 170°F, however, during squeeze-cementing operations in formations of high thermal conductivity it is difficult to see why the slurry would not reach approximately the (subsurface) formation temperature."

From the results of a study by Bogue and Lerch[9] it was suggested that the cause of the initial set may be the formation of either hydrated tricalcium aluminate ($3CaO \cdot Al_2O_3$, or C_3A for short) or hydrated tricalcium silicate ($3CaO\ SiO_2$, or C_3S for short). The time required for the initial set appeared to be governed by the time necessary for one or the other of those hydrates to appear. When no

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[8] Neighbors, G. R. and Cromer, S., Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1399 (Petroleum Technology), 4, No. 6, 5, (1941)

[9] Bogue, R. H. and Lerch, W., Research Reports, Portland Cement Assoc. Fellowship Nat. Bur. Standards, Sept., 1933.

retarder was present, or when the C_3A content was high, the C_3A went into solution and the C_3A hydrate formed very quickly, according to the following reaction:

$$3\ CaO \cdot Al_2O_3 + n\ H_2O \rightleftharpoons 3\ CaO \cdot Al_2O_3 \cdot nH_2O \text{ ------ (1)}$$

This formation may be great enough to produce rigidity of the cement, in which case it is said to have a flash set. In this case the precipitating C_3A hydrate established the structure of the cement paste formed. But if the C_3A content were low, or if a retarder were present to delay the precipitation of its hydrate, then the more slowly reactive C_3S would have time to dissolve and precipitate as C_3S hydrate, as shown below:

$$3\ CaO \cdot SiO_2\ (s) + n\ H_2O \rightleftharpoons m\ CaO \cdot SiO_2 \cdot nH_2O + (3-m)\ Ca(OH)_2 \text{ ------ (2)}$$

In that case the C_3S hydrate would establish the set and the structure of the paste, and the time of set would be normal.

The presence of calcium sulfate was found to cause a reaction with the C_3A and $Ca(OH)_2$ in solution to form calcium sulfoaluminate, which is only slightly soluble. The reaction in the presence of an aqueous medium is

as follows:

$$3\ CaSO_4 + 3\ CaO \cdot Al_2O_3\ (s) \rightleftharpoons 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O \quad (3)$$

The effect of this reaction was to reduce the concentration of C_3A in solution below the point where C_3A hydrate could separate out. This process would continue until either the $CaSO_4$ or the C_3A were exhausted, and during this period the C_3S could hydrate as if in the absence of C_3A. When the $CaSO_4$ was depleted the remaining C_3A could hydrate, but it would precipitate within the structure established by the C_3S.

This all suggested that a normal retarded set is due to the hydration of the C_3S, requiring a number of hours to proceed to the point of rigidity in usual cases. But the very rapid reaction of C_3A with water may bring about a flash set if it is not retarded by some agent, such as $CaSO_4$, which will suppress its normal hydration.

It should be noted that the use of gypsum, $CaSO_4$, is common to all Portland cement, since it is necessary to provide any reasonable retardation of the initial set at all conditions of temperature. If further retardation is desired, as in the case of high-temperature oil wells, additional retarding agents must be added. The amount of retardation provided by the gypsum depends upon its degree

of hydration, as added to the cement clinker at the factory. In its usually-added form as the dihydrate, $CaSO_4 \cdot 2H_2O$, the optimum amount is about 2.0 per cent by weight.

CHAPTER III

RESUME OF LITERATURE ON ADDITIVES

Many investigators in the past have proposed numerous chemical additives or special treatments for the further specific retardation of oil-well cement. A literature study has been conducted in an effort to locate all important references to such cases. Special attention was paid to materials or processes listed in the patent literature.

Some of the more important additives that have been used are listed in Table II, along with data illustrating the test results obtained with the use of each.

TABLE II

PAST USE OF CHEMICAL ADDITIVES

Additive, and % Used (by wt. of dry cement)	Test Temp. °F	Stiffening Times In Hours, To Indicated Consistency in Poises.	% Increase Over Similar Stiffening Time For Plain Portland Cement at the same Temp.
NO_2-oxidized cellulose (OC)			
0.09 %	140	13.10 hrs. to 100 p.	285.0
"	180	13.50 hrs. to 100 p.	638.0
"	200	6.78 hrs. to 100 p.	338.0
"	220	2.02 hrs. to 100 p.	68.3
"	220	3.68 hrs. to 100 p.	207.0

TABLE II (continued)

Additive, and % Used (by wt. of dry cement)	Test Temp. °F	Stiffening Times In Hours, to Indicated Consistency In Poises	% Increase Over Similar Stiffening Time for Plain Portland Cement At the Same Temp.
K salt of OC			
0.10 %	200	4.52 hrs. to 100 p.	191.6
NH_4 salt of OC			
0.10 %	200	5.88 hrs. to 100 p.	279.5
Maleic Acid			
0.30 %	100	11.92 hrs. to 100 p.	78.0
"	140	4.78 hrs. to 100 p.	59.4
"	180	4.17 hrs. to 100 p.	106.4
"	200	10.13 hrs. to 100 p.	469.0
"	220	4.87 hrs. to 100 p.	218.0
Modified Starch			
0.12 %	100	8.75 hrs. to 100 p.	30.6
"	140	9.03 hrs. to 100 p.	201.0
"	180	10.08 hrs. to 100 p.	399.0
"	200	6.72 hrs. to 100 p.	261.0
"	220	2.80 hrs. to 100 p.	83.0
Carboxy methyl cellulose (CMC)			
0.30 %	200	7.10 hrs. to 80 p.	915.0
Na salt of CMC			
0.24 %	140	2.88 hrs. to 80 p.	33.9
"	180	3.60 hrs. to 80 p.	63.7
"	200	5.35 hrs. to 80 p.	664.0
"	220	6.96 hrs. to 80 p.	1212.0

According to Mr. N. C. Ludwig* of the Universal Atlas Cement Company, the only additives in commercial use today are the following:

(1) carbohydrates such as modified starch and sugar,

(2) calcium and sodium salts of lignin sulphonic acid.

CHAPTER IV

PRINCIPLES OF MEASUREMENT OF CONSISTENCY

As mentioned in the introduction, when any cement is tested for possible use in oil wells, it should be done under special temperature and pressure conditions which should approximate those expected to be found in the wells. These tests should measure the mobility of the cement. Consistency, which is the term used for the viscosity of a cement slurry, is the property which can be easily measured in the laboratory and bears the most direct relation to mobility.

The object of the consistometer tests was to measure the consistency of the cement slurries through the range of possible field usage. In this manner data could be obtained from which could be predicted the performance of the cement when it is pumped into a well under similar temperature conditions. And from these data the allowable time that the cement could be pumped at a given temperature could be predicted. The practical importance of such a consistometer apparatus in providing data for the evaluation of cement slurries has been emphasized in various technical

publications by such investigators as Davis[10] and Weiler.[11]

The time that a cement slurry can be stirred before rapid stiffening occurs is partially dependent upon the rate of shear. The rate of a chemical reaction between liquid and solid phases always increases with increase of agitation, consequently, the rate of setting should increase with the rate of stirring. Therefore, a constant rate of shear was used for all test runs, the speed of the consistometer rotation being 43.8 r.p.m. The Halliburton Consistometer turns at about 25 r.p.m. and the high-pressure consistometer described in the results of test investigations by Farris[12] turned at 47 r.p.m.

Units of measurement of viscosity properly apply only to truly viscous fluids, but a cement slurry is not a true viscous fluid. However, the resistance to shearing agitation offered by a cement slurry can be conveniently measured in the experimental consistometer, since this machine measures directly the viscosity of a true viscous fluid. Hence, the word, consistency, will be the special name applied to the viscosity of a cement slurry, in poises, to distinguish it from that of a true fluid.

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[10] Davis, E. L., Calif. Oil World 31, No. 13, 14, (1938).

[11] Weiler, J. E., Petroleum Engr. 9, No. 12, 33-4, (1938).

[12] Farris, R. F., Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1207 (Petroleum Development and Technology) 142, 119. (1941).

Even though cement slurries are not true viscous fluids, it is the practice in industry to calibrate the consistometer with a true viscous fluid, and that was done in this investigation. This calibration procedure is described in Chapter VII. The experimental apparatus for the measurement of consistency was patterned after a commercial machine, the Halliburton Consistometer, which is essentially a modified Stormer Viscosimeter. In reference to its construction, it is said to be of the "ice-cream freezer" type, because of the paddle-like stirrer blades inserted in the slurry chamber, or can. Details of construction can be found in Chapter V.

Temperature and pressure have their own separate effects on the setting characteristics of the cement. It is definitely known that increase in either temperature or pressure will accelerate the setting, and vice versa. A graphical representation of these phenomena is shown on Figure 4. It may be seen from this plot that an increase in temperature has a greater effect on the setting rate than does an increase in pressure.

In 1941, Neighbors and Cromer,[13] reporting on "Some Factors Controlling the Pumping Time of Oil-well Cements,"

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[13] Neighbors, G. R. and Cromer, S., Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1399 (Petroleum Technology), 4, No. 6, 5, (1941)

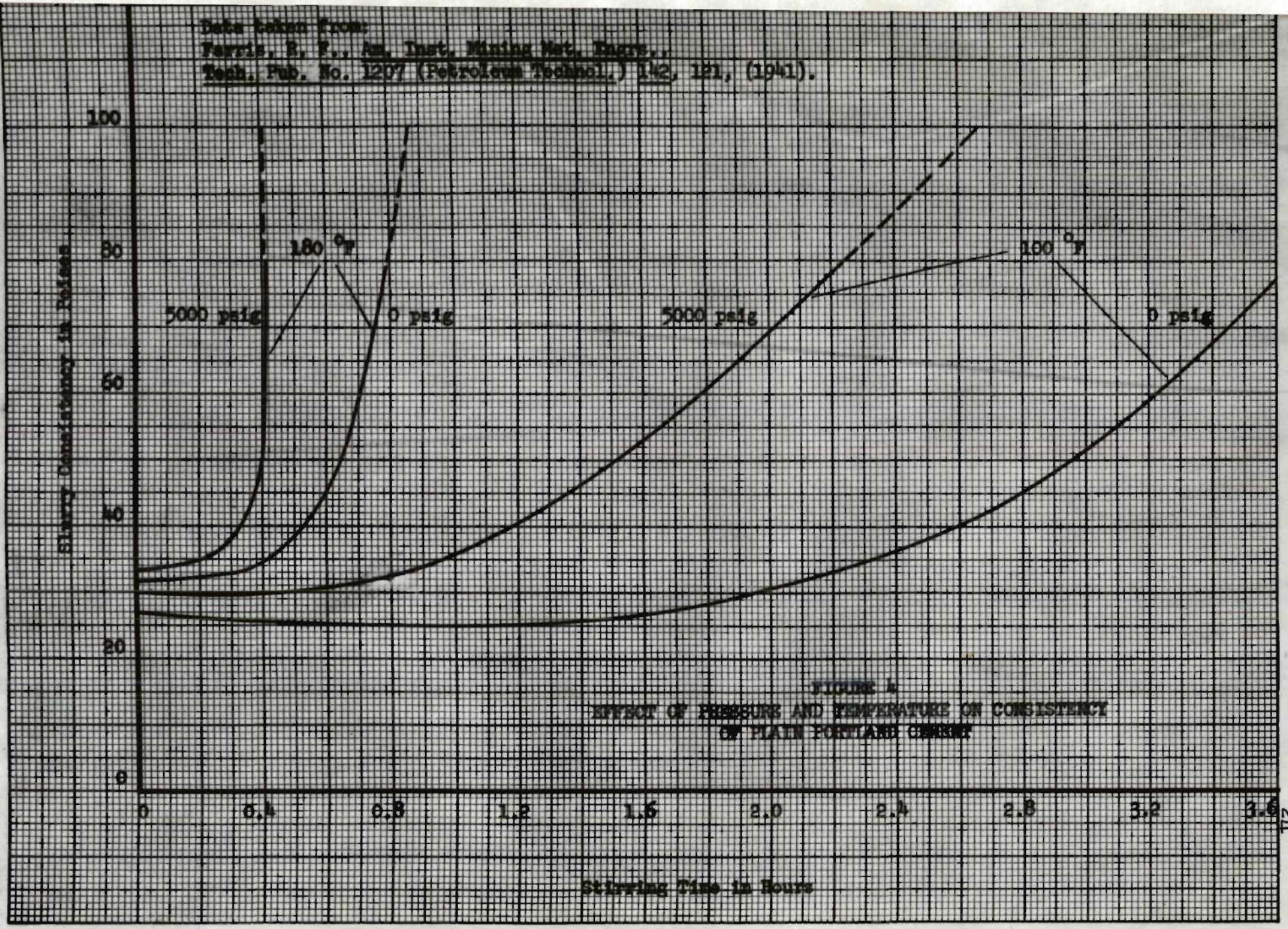

FIGURE 4
EFFECT OF PRESSURE AND TEMPERATURE ON CONSISTENCY OF PLAIN PORTLAND CEMENT

gave some very interesting test results. Their investigations were conducted with three commercial brands of cement from the Universal Atlas Cement Company, the Trinity Portland Cement Company and the Lone Star Cement Company. Their conclusions were, that, of the four variables affecting the fluidity of cement slurries, temperature is the most important controlling factor. The variables,listed in order of importance, are:

(1) Temperature

(2) Pressure

(3) Water-cement ratio

(4) Storage time

The experimental equipment used in this investigation was designed to test only the effect of temperature at atmospheric pressure. It was realized before the testing began that such results as would be obtained could not be a complete picture of the situation, comparable to oil-well conditions, with the effect of the pressure variable lacking. Since this was only a preliminary investigation of the problem, it was felt that the construction of a pressure-testing apparatus was unnecessary and too expensive. However, it was thought that the results obtained in temperature tests at atmospheric pressure could be extrapolated, with some degree of certainty, to apply in like manner at higher pressures.

Then a chemical substance which retarded the setting of cement at low pressures would also retard at high pressures, though, probably its effectiveness would be lessened.

The validity of this assumption has been borne out by a past investigator, Farris,[14] whose test results are shown on Figure 5. In this figure a comparison is made between plain Portland cement and a commercial oil-well cement and it is obvious that the retarded oil-well cement is better than the un-retarded Portland cement, regardless of the pressure involved. The stirring time of both cements decreases linearly with an increase in pressure.

It is common practice in the cement industry to compare cement slurries at some common consistency in order to evaluate the relative abilities of the different cements to remain as pumpable slurries for a time sufficient to allow proper placement in a cementing operation. For the test results to have the greatest practical significance this consistency should be equal to the maximum practical slurry consistency that can be handled by the cement pumps. The experimental stirring time will probably bear a definite relation to the time that a cement slurry may be pumped, other variables being held constant.

Previous investigators, using consistometers that

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[14] Op. cit., 123.

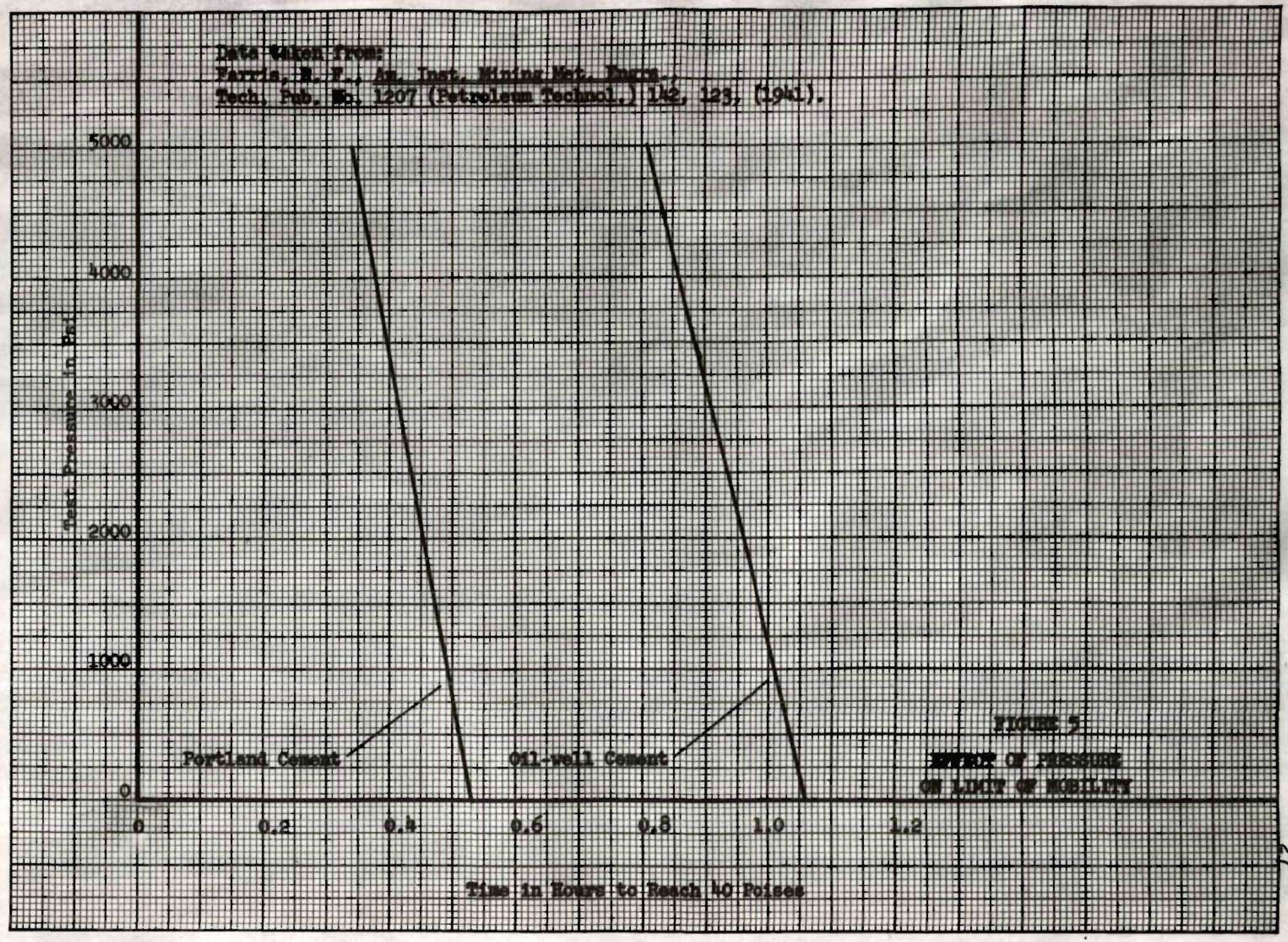

FIGURE 5

EFFECT OF PRESSURE
ON LIMIT OF MOBILITY

operated at atmospheric pressure, suggested that a slurry consistency of 40 poises be used as the experimental limit of mobility. And the manufacturers of the Halliburton Consistometer, as well as the manufacturers of the particular cement used in this investigation, agree that 40 poises should be the hypothetical limit of mobility for cement tested in this type of machine.

In all cases where the stirring was stopped before the consistency reached 100 poises the data were extrapolated to 100 poises in plotting. The time required to reached this point is sometimes referred to as the "stirring time" of a cement slurry and as such is used as a basis for comparisons of various cements. Cement slurries of a consistency more than 100 poises can not be moved successfully by a pump, regardless of the pump pressure, so it is usually pointless to continue stirring of a cement slurry until such a consistency is reached.

Stopping of the stirring at a lower maximum consistency may be desirable from another standpoint. Farris[15] has pointed out that the strength of a set cement was not greatly affected by stirring or agitation while the slurry was fluid, but that the strength of the set cement was definitely injured if the slurry was stirred or otherwise

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[15] Op. cit., 124.

strongly agitated after starting to stiffen. His results also showed that the rate of strength reduction from agitation increased as the rate of stiffening increased. A graphical representation of his test results leading to this conclusion are shown on Figure 6. From the implications of this graph it would seem wise to discontinue stirring at a maximum consistency of 50 poises, if the set cement were to have any reasonable degree of strength, so as not to lose all the advantages gained in the use of slow-setting cement. Certainly a cement slurry consistency sufficiently low to permit placement is the first requisite, but other qualities such as the strength of the set cement, uniformity of the slurry, and the ability of the slurry to displace drilling fluids properly should also be taken into account.

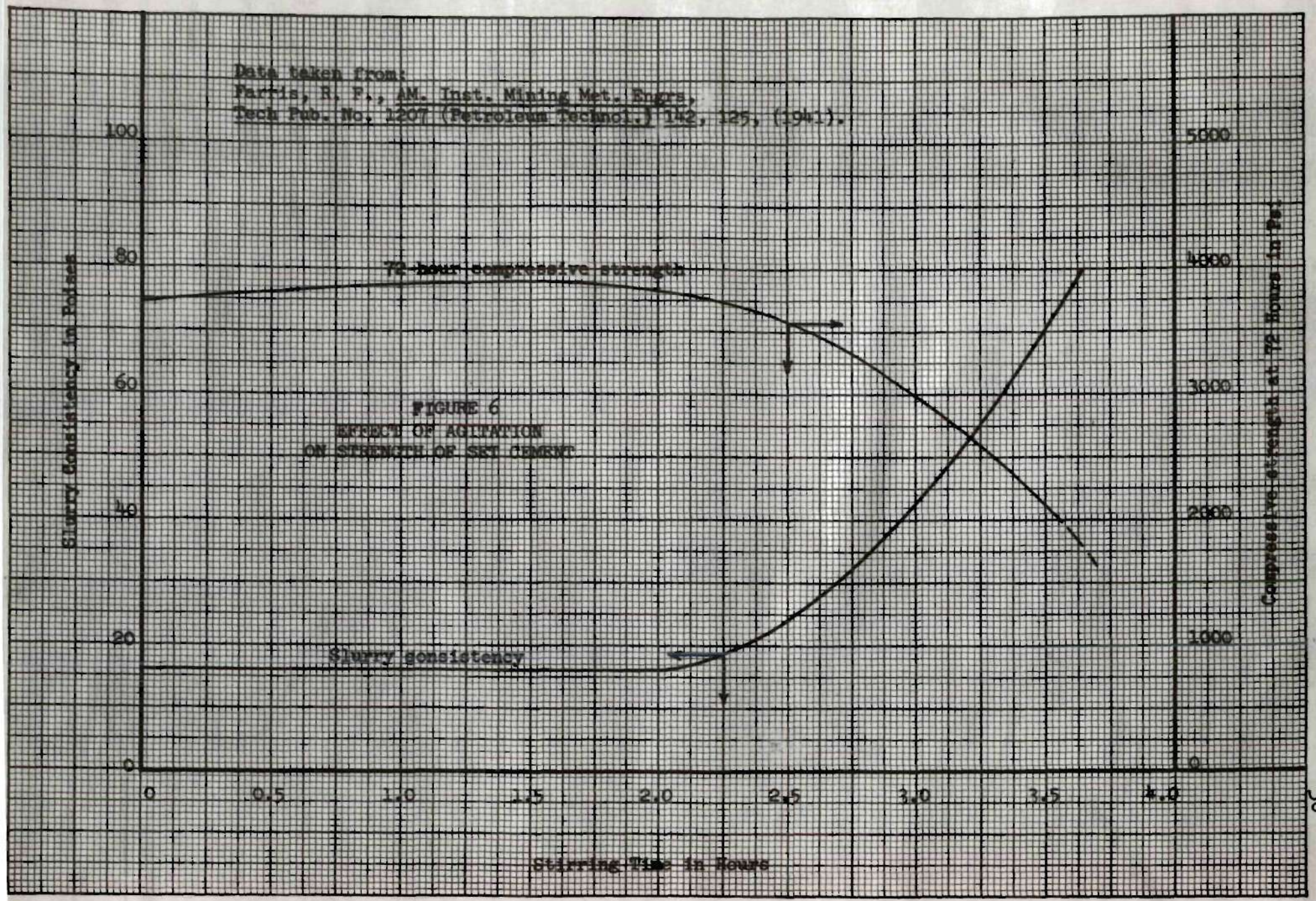

FIGURE 6
EFFECT OF AGITATION
ON STRENGTH OF SET CEMENT

CHAPTER V

EXPERIMENTAL EQUIPMENT

An overhead view of the experimental consistometer is shown on Figure 7. A is the water-bath compartment and it serves to keep the slurry chamber, or can, B, at a constant temperature throughout a test run. The visible part of the can is a flat-plate worm-gear, with an underneath recess, machined so that it bolts over the flanged top of the can. It is rotated by the worm, C, which in turn is driven by a 1/6 H.P. electric motor, D. To insure an even distribution of temperature in the bath, the water was re-circulated by the electric-driven centrifugal pump, E, at a capacity of 3 g.p.m., insuring a complete change of all the bath water at least once every two minutes, the bath capacity being about 5.6 gallons. The bath water was heated by a submerged electric-resistance heater, or calrod. The external connections to this 1000-watt heater are labeled as points F,F on the photograph. The temperature control on the heating system was accomplished by an electric thermo-regulator and magnetic-relay system connected in series with the heater circuit, all functioning from the same supply of 110-volt, 60-cycle alternating current. The thermo-regulator is signified by G and the relay is at H.

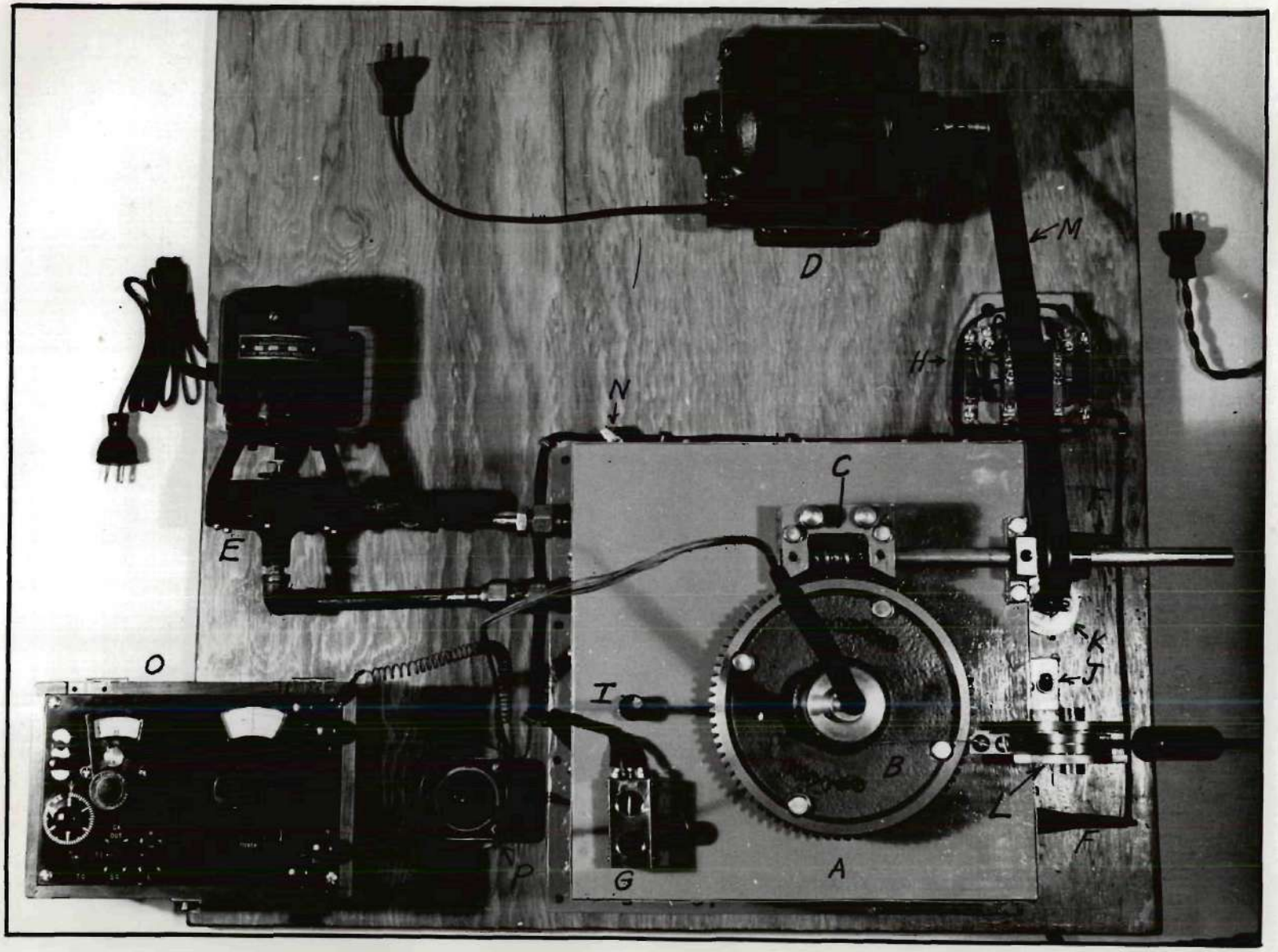

FIGURE 7 EXPERIMENTAL CONSISTOMETER APPARATUS

Part I is the mercury-in-glass thermometer for water-bath temperature. It is inserted through a one-hole rubber stopper which is fitted into a tapered hole in the top of the bath container, this latter hole serving as a filling point for the bath water. J indicates the calrod heater switch, where the power supply can be controlled manually if necessary, and K is a neon-glow pilot lamp, connected in parallel with the heater, to give a visual indication when the heater is on. The torque-indicating assembly, which measures the consistency, is shown by L and the motor pulley-drive V-belt is part M. The small part, N, just barely visible at the lower-left rear corner of the bath is a $\frac{1}{4}$" drain cock.

The other instruments in the picture comprise the temperature-measuring system of the consistometer, registering the temperature at four different points in the can, by means of thermocouples. The instrument, O, is a portable, double-range potentiometer indicator, connected through the selector switch, P, to allow it to read, successively, any of the four temperatures at the thermocouple junctions. An enlarged view of this temperature-indicating system is shown on Figure 8.

The stirrer shaft, 1, is a hollow, stainless-steel tube, with the four, iron-constantan, thermocouples inside, their junctions being soldered at the furface of the tube,

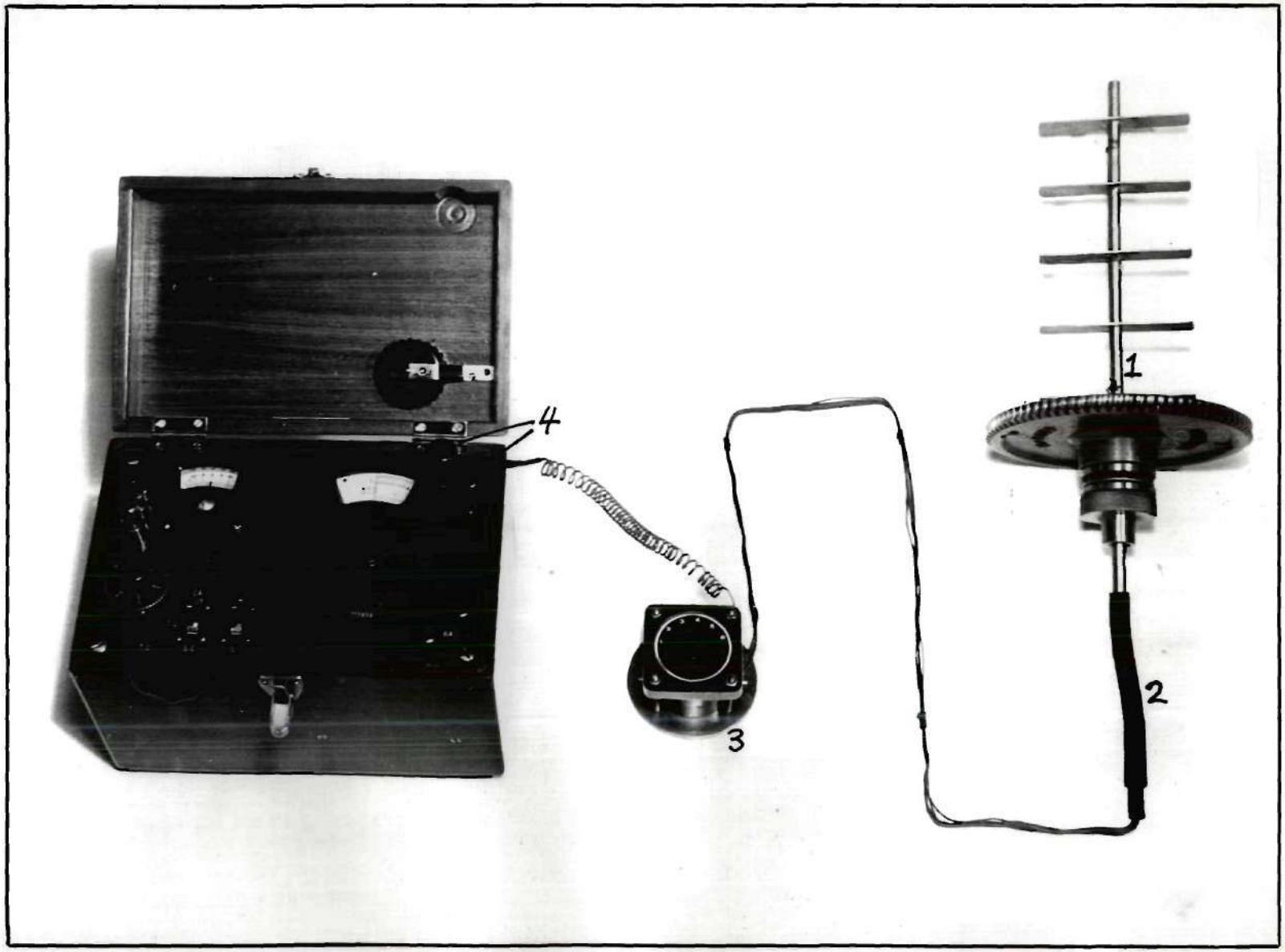

FIGURE 8 POTENTIOMETER-THERMOCOUPLE TEMPERATURE INDICATOR

in four different locations across the length of the tube. This enabled a check to be made for any temperature gradient that might exist in the cement, when placed in the can and running. The thermocouple wires passed up through the tube, through an insulating, protective rubber tube, 2, through the five-point selector switch, 3, and then to the terminals of the potentiometer, 4, 4. This setup was used on the first test runs of the apparatus but when it was found that there was no significant difference in the temperature between any of the four positions, it was discarded in favor of a mercury-in-glass thermometer (not shown) which was immersed in oil in the hollow-tube shaft. The thermometer was much simpler for the purpose of taking readings and was used throughout the testing period after the initial calibration of the consistometer.

The operation of the consistometer can be understood more easily by referring to Figure 9. The cement slurry is placed in the slurry chamber, or can, a, which passes through the round hole in the top of the water-bath case, b, and rests upon a pivot-bearing socket (not visible) which is suspended inside the bath case. The stirrer, c, is a hollow steel tube with flat brass blades soldered to it. The lid of the can, d, when screwed into place, engages with the worm, e, which is turned by the motor-driven shaft, f. As this shaft turns it causes the can to revolve in a clockwise

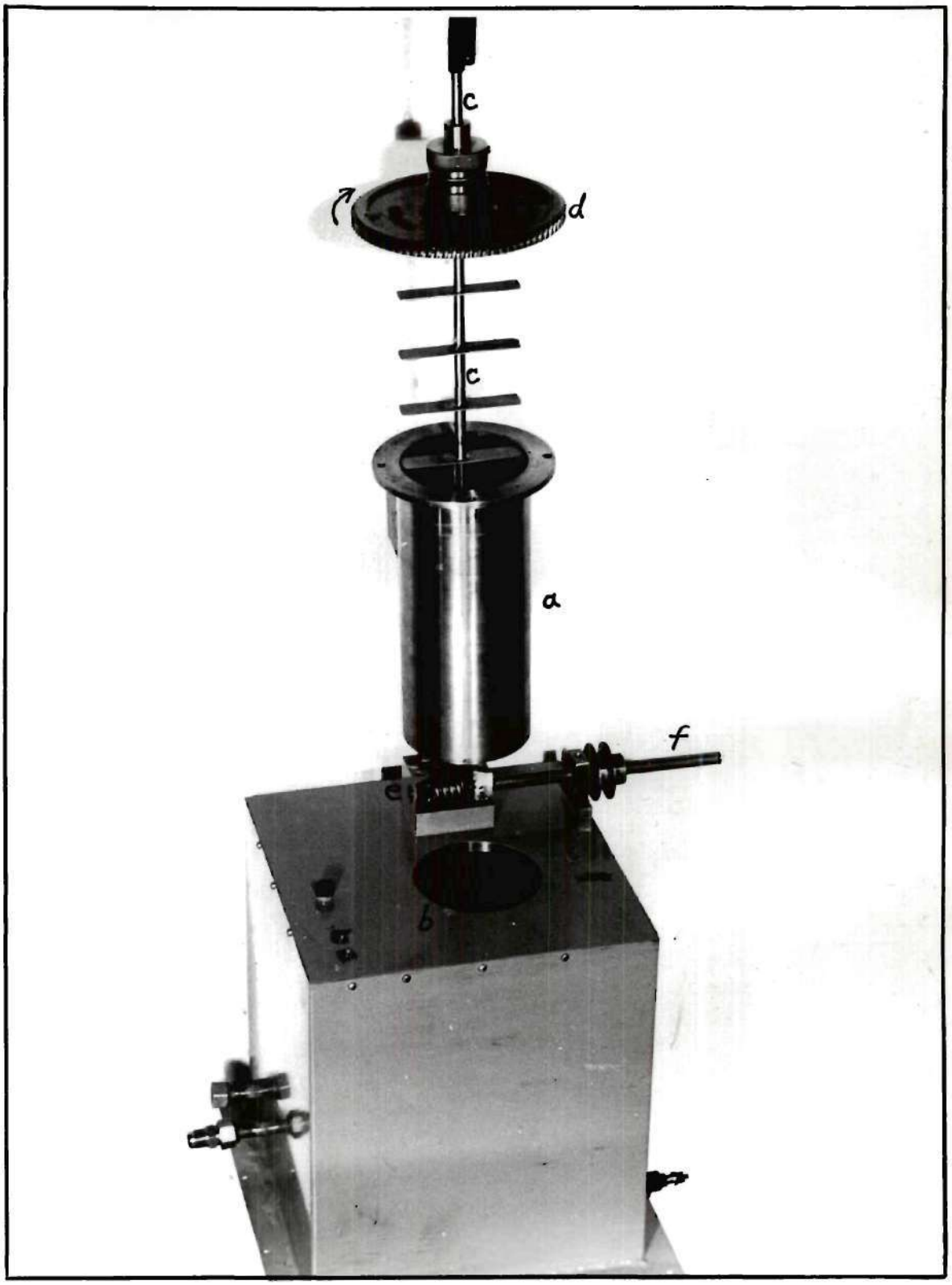

FIGURE 9 CONSISTOMETER CAN AND STIRRER

direction, reading from above. As the can revolves it pulls the thick slurry around with it, causing the cement to impinge upon the stirrer blades with a shearing action. The natural tendency of these blades is to follow the direction of can-revolution, since they are supported through a cylindrical collar on a ball bearing. A close-up view of this bearing-support assembly is shown on Figure 10.

The lower race of this bearing, g, is fitted to the top of the can so that it revolves with the can. At the same time the upper race of the bearing, h, supports the collar, i, allowing the stirrer to ride easily, with very little friction, since it is clamped inside the collar with two set-screws. But the collar is also connected to a torque-indicating assembly with a small length of braided fishing line, j. As the collar tends to revolve it is held back by the pull of the torque-indicating assembly. A pull on the line, in the direction shown by the arrow, will rotate the torque shaft, k, in the direction shown, and cause the sliding weight, l, positioned on the moment arm, m, to be lifted toward a horizontal position.

This torque-indicating mechanism is very reliable and the inherent inaccuracies of springs, so often used in graduated pull-indicating devices, are avoided by using this simple pendulum-like construction. As this pendulum is pulled from the vertical, "at-rest," position a moment is

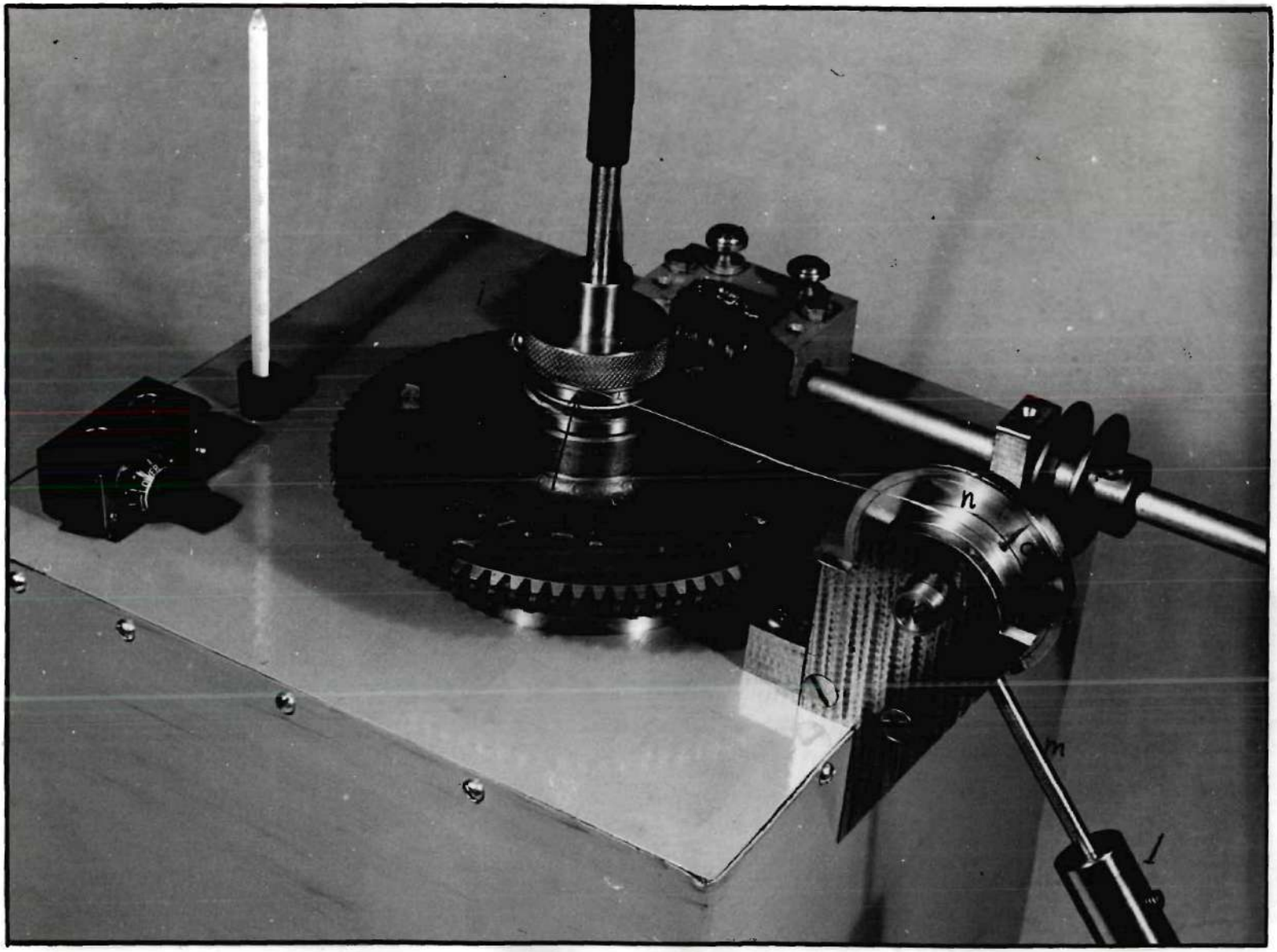

FIGURE 10 TORQUE-INDICATING DEVICE FOR CONSISTENCY MEASUREMENTS

created. The value of the moment varies from zero to a value equal to the weight of the moment arm and the weight, l, multiplied by the perpendicular distance out to the center of gravity of the sliding weight and the moment arm, both considered as a unit. The quadrant scale, n, behind the scale pointer, o, is graduated in ten equal increments of torque, although the angular distance between successive graduations varies. Each of the graduations represents 10 units of consistency, or poises, and they were located by calibration as described in Chapter VII.

The speed of revolution of the can is determined by the speed of the driving motor and the reduction ratio of the worm and worm-gear unit. The motor turned at a speed of 1750 r.p.m. and the reduction ratio of the gear unit was 40 : 1, therefore,

$$\text{Stirring speed} = \frac{1750}{40} = 43.8 \text{ r.p.m.}$$

Since the cement was to be tested for compressive strength after it had set, some method had to be devised for molding and curing the cement, that is, keeping it completely moist, at the test temperature, until such time as it was ready to be crushed in the hydraulic compression tester. For this purpose, the large, enclosed curing bath, shown on Figure 11, was built.

It consits of a galvanized, sheet-steel tank, A,

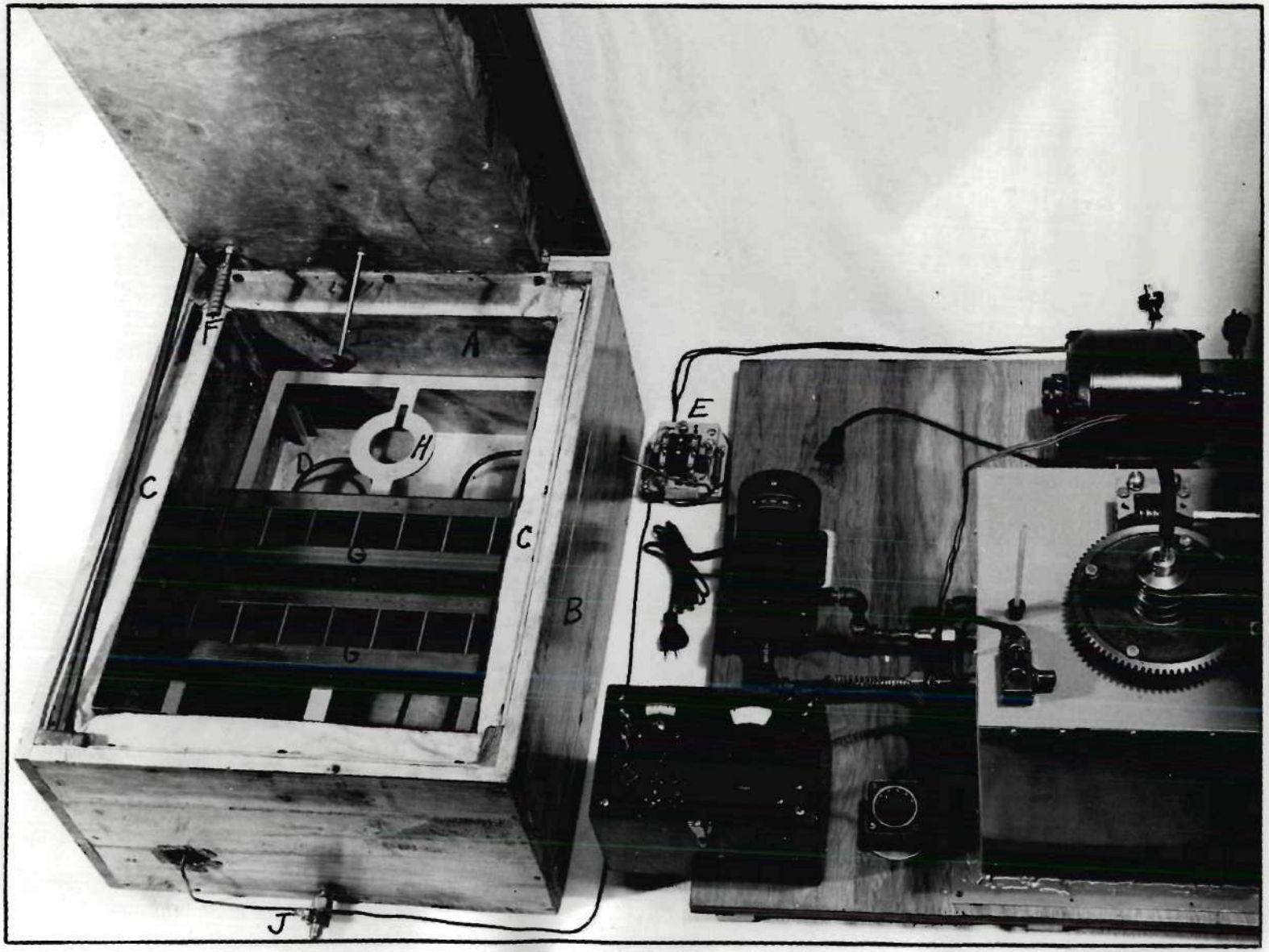

FIGURE 11 CEMENT-CURING BATH AND COMPRESSION MOLDS

surrounded by a larger wooden case, B, Between the case and the tank powdered magnesia and asbestos fibre, C, were packed to insulate the system against heat loss. Since the bath was heated by a submerged electric calrod, this insulation allowed the bath to hold more closely to a prescribed temperature without keeping a continuous high load on the heating-relay circuit. The calrod, D, rated at 750 watts, and the magnetic relay, E, were in series circuit with a thermo-regulator, F, and all were operated from a single source of 110-volt, 60-cycle alternating current.

The cement molds, G, were placed on a submerged steel rack, H, and allowed to remain there during the curing period, which was 23¼ hours. A propellor-stirrer, I, was used to agitate the bath water, insuring an even temperature distribution. It was driven by a small electric motor (not visible) mounted atop the lid of the wooden case. A mercury-in-glass thermometer (not shown) was mounted in a metal sheath-tube which passed through the lid of the case, enabling the operator to observe the bath temperature without opening the case. Part J is a 3/8" drain cock.

The device used to test the molded cement dubes in compression was a Riehle Model "505" Universal Hydraulic Testing Machine. A picture of the machine is shown on Figure 12. It is an oil-driven cylinder and plunger type tester with a capacity of 60,000 lbs. The test cubes, 1,

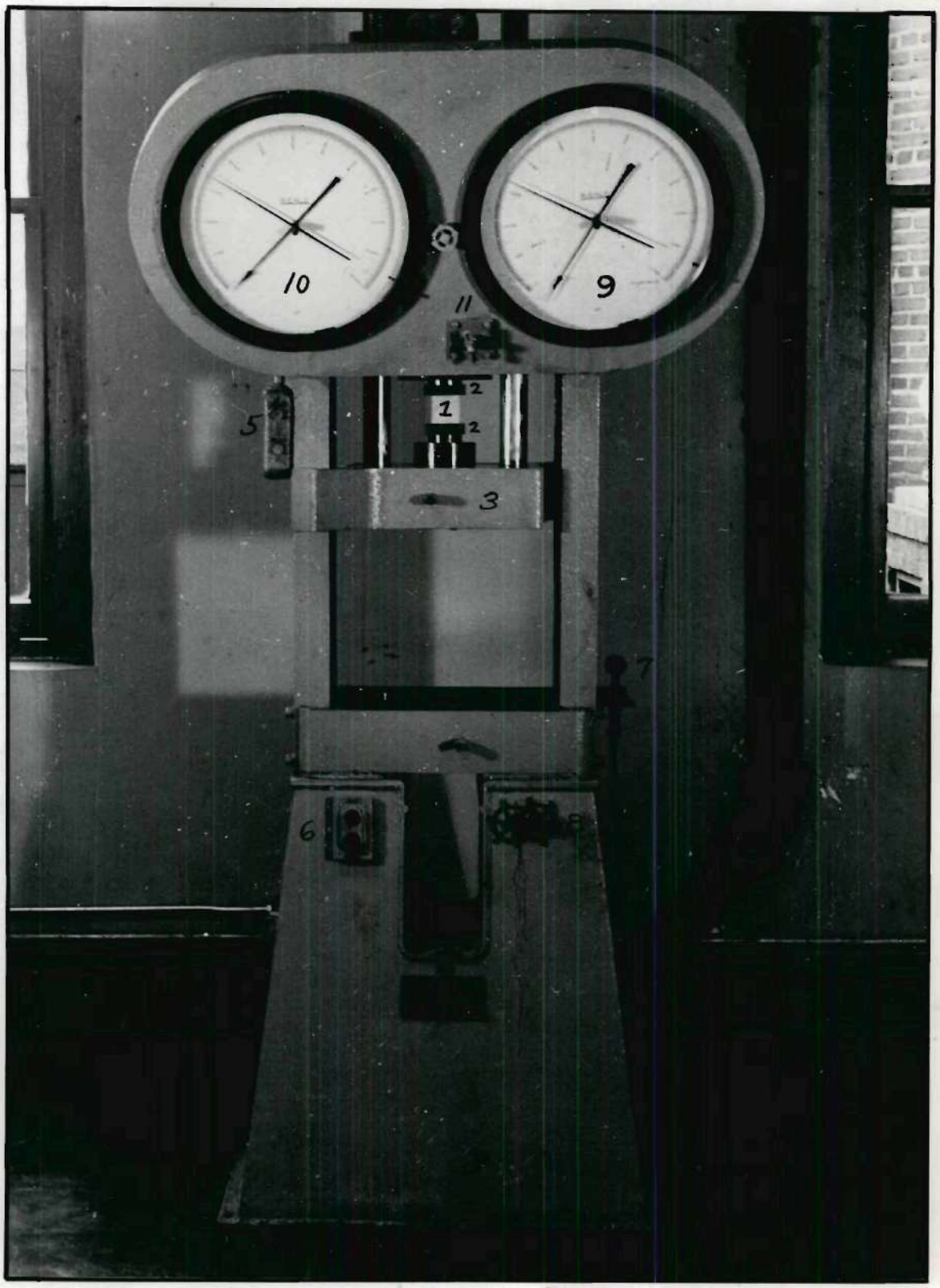

FIGURE 12 RIEHLE COMPRESSION TESTER

were placed between the platens, 2,2, and the pulling head, 3, was raised by its motor, 4, which was controlled by the switch, 5. When the upper platen was seated firmly against the cube, the hydraulic pump motor (not visible) was started with the switch, 6, thereby raising the pulling head very slowly, to compress the cube between the platens. The speed of the compression drive was controlled by the lever, 7, which throttled the pump. The valve, 8, was used to control a bypass line on the pump and it was kept closed when the pump was driving. The pressure gauges at the top of the machine indicate the total pounds force being applied to the cube, dial 9 reading to 12,000 pounds and dial 10 reading to 60,000 pounds. The valve, 11, was used to shut off the oil line to dial 9 when the pressure neared 12,000 pounds, the maximum pressure it would withstand.

CHAPTER VI

EXPERIMENTAL MATERIALS

The cement used in this investigation was plain, gray Portland cement, made by the Universal Atlas Cement Company, and specified as ASTM Type I. It was kept stored in an airtight fibre-board drum or in smaller, airtight cans. All samples were passed through a standard 840-micron (No. 20) sieve before mixing into slurries, and the average amount retained on the sieve was weighed and found to be 1.562% of the total weight sampled, as specified in the ASTM standards.[16] The cement was sampled, originally, from each of five 94-lb. sacks, taking the samples in rotation to insure a fair, representative cross-section of the whole lot. The sampling tube was made of copper, according to the API Code. Hereinafter, when this code is mentioned it refers to Tentative Code No. 32 for "Testing Cements Used in Wells," American Petroleum Institute, Division of Production.

The mixing water for the slurry was distilled water, as specified by API Code 32 for reference tests on cement. It was stored in a 5-gal. glass bottle with siphon tubes, and was kept CO_2-free by an absorption tube filled with

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[16] Am. Soc. Testing Materials, Standards. Part II, 18, (1939).

NaOH pellets and glass wool.

The first test material investigated as a retardant was sodium pyrophosphate-decahydrate, $Na_4P_2O_7 \cdot 10H_2O$. It was from a standard laboratory supply bottle, Baker C. P. Laboratory Chemicals, Lot No. 12341, and was labeled 99.97% pure, containing impurities in the following amounts:

Cl	0.001 %
SO_4	0.005 %
Fe	0.004 %
Insol.	0.020 %

The second test material investigated as a retardant was quebracho. It is prepared by hot-water or alcohol extraction from the wood of the South American red quebracho tree (Quebrachia lorentzii). The samples used were taken from an unanalyzed lot of the commercial-grade extract and were found to contain a few traces of insoluble matter that appeared to be small grains of sand, or possibly, wood fiber.

These two retardant materials were first considered as being possibly suitable because of their past successful usage as viscosity-reducers for the drilling muds used in oil-well operation.

CHAPTER VII

CALIBRATION OF THE CONSISTENCY SCALE

The consistometer can was filled to the prescribed level with the calibration fluid, Paratone, which is a very heavy solution of a hydrocarbon polymer in mineral oil, purchased from the Refinery Supply Company, Tulsa, Oklahoma. The viscosity of this fluid with temperature is accurately known over a range of 6-180 poises, as shown in Figure 13. From this graph the temperature was chosen at which the viscosity of the Paratone would be 100 poises. Then the temperature control system was set to maintain the consistometer water bath at this temperature, 96.4°F. Temperature control was maintained here to an accuracy of $\pm$ 0.05°F. As soon as the heat was turned on, the stirrer motor was started and the can was continuously revolved until the temperature of the Paratone was the same as that in the bath. Then the sliding weight was adjusted until the moment arm was exactly horizontal, the point at which the maximum moment could be recorded. This position was selected so that the greatest distance possible would be achieved between graduations on the quadrant scale, since 100 poises was to be the limit of the test range.

When the machine was running steadily at constant

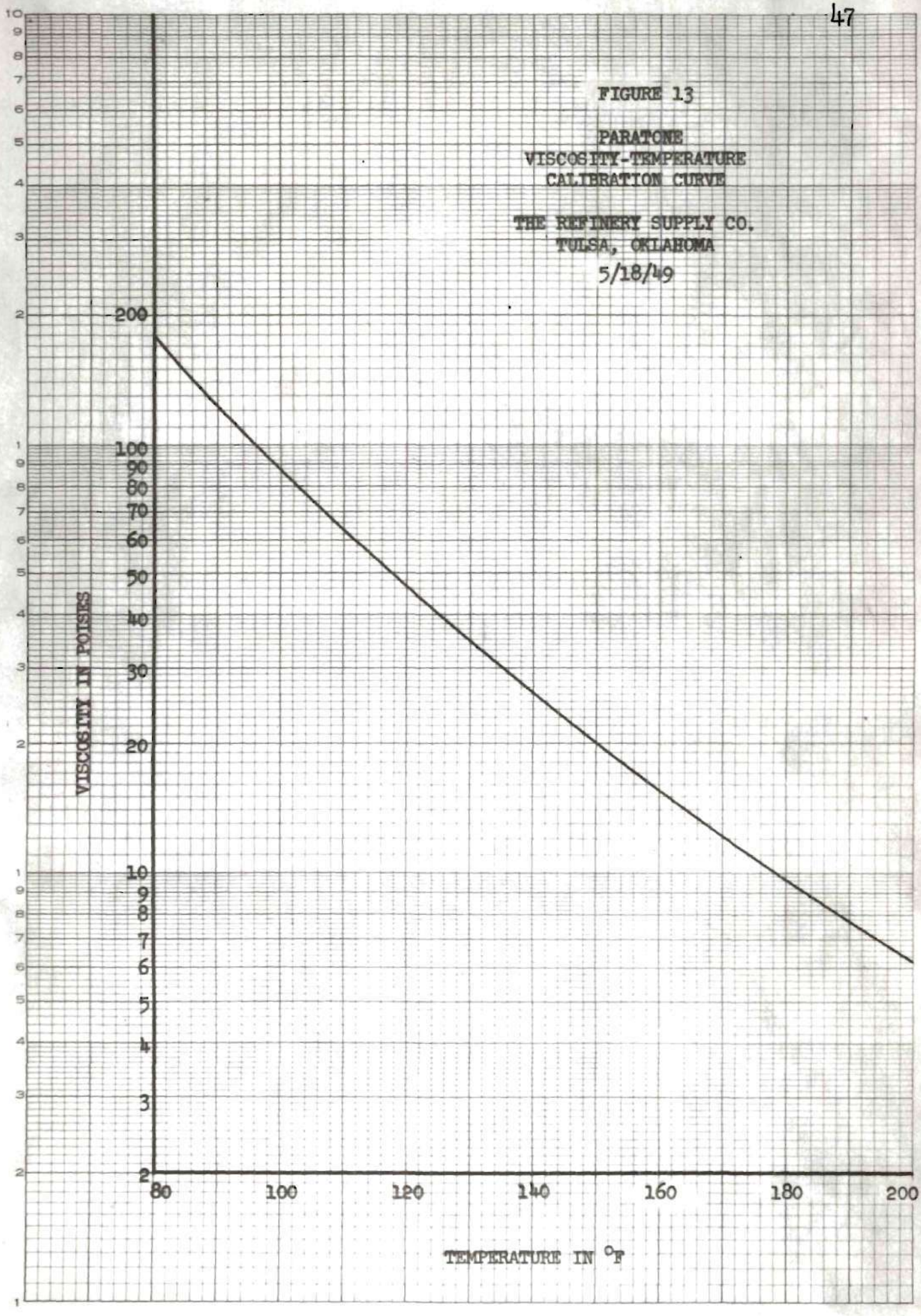
FIGURE 13
PARATONE
VISCOSITY-TEMPERATURE
CALIBRATION CURVE
THE REFINERY SUPPLY CO.
TULSA, OKLAHOMA
5/18/49
VISCOSITY IN POISES
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
80
100
120
140
160
180
200
TEMPERATURE IN °F

temperature the position of the pointer for 100 poises was marked on the scale. Then the same operation were repeated for all temperatures that corresponded to successive, decreasing intervals of 10 poises, until the position for 10 poises had been reached. Then the machine was stopped, the can emptied, and the moment arm allowed to hang free. At this position, the scale was marked for 0 poises.

When the can is filled with cement in an actual test run the slurry will affect the positioning of the moment arm just as the Paratone did. As previously mentioned, the slurry tends to drag the stirrer along as it revolves, but the stirrer is held back by the weight of the moment arm. Consequently, the stirrer blades cut through the cement with a shearing force that is proportional to the consistency of the slurry. Since the quadrant scale has been calibrated, the position of the pointer is a direct indication of this consistency, measured in poises. As the slurry increases in thickness the stirrer blades continuously take a gradual rotation in the direction the can is turning, while the cement is cutting past their relatively stationary position. Since the moment arm is tied directly to the stirrer-shaft collar it is constantly lifted toward the horizontal, its increasing elevation corresponding directly to the change of consistency of the slurry. Because the calibration was based on units of shearing force it holds

true for any fluid that may be tested, so long as the viscosity of the fluid, at the temperature being used, falls in the applicable range of the scale (0-100 poises).

CHAPTER VIII

EXPERIMENTAL PROCEDURE

The API Code 32 specifies that the weight of water added to the cement being tested shall be a constant percentage by weight of dry cement used. The percentage varies with the type of cement, according to the fineness, and the specifications call for 46.0% to be used with Type I Portland cement. However, since the Portland cement used was being tested for its operability as an oil-well cement, the test slurries were made up using 40.0% water, which is the amount[17] specified for slow-set or oil-well cements. This means that 40 grams of water are required for each 100 grams of dry cement.

Likewise, the chemical retarding agents were proportioned on the same basis, that is, percent by weight of dry cement. However, it is the practice of the field cementing operators to calculate their slurry thicknesses, or weights, in pounds per gallon, and these in turn are reported in barrels of slurry pumped. It is well to have a measure of the amount of additive on this basis, therefore the amounts of retardants added were also calculated in terms

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[17] API Code 32, p. 5.

of pounds per barrel of slurry. These calculations are all illustrated in Appendix D.

The cement was weighed out in 1000-gram lots, and fractions thereof, on a single-beam trip scale using brass counterweights, to an accuracy of ± 0.20 grams. It was weighed out into a tare-balanced brass scoop and then transferred to an enamel pan so that all of it could be easily mixed with the water. The mixing water was weighed out directly in the tall steel can used for a mixing vessel, on the same scales used for the cement, and to the same accuracy. The chemical retardants were weighed on a chainomatic, double-pan, analytical laboratory balance, to an accuracy of ± 0.0001 gram, and then added directly to the mixing water.

It will be noted in Appendix B that, starting with Run No. 4, the amount of slurry was increased so that the can could be filled more quickly and still leave some slurry to spare.

The following description of the operations performed during a consistency test run are based on Run No. 9, the first in which quebracho was used as the retardant. The run made with sodium pyrophosphate-decahydrate was similar in every detail, with the exception of the amount of retardant sample used. The runs made with plain Portland cement were similar except that no retardant was added. Wherever practicable,

the experimental procedures followed the specifications of the API Code 32. The steps in the test run, up to the introduction of the molded samples of cement into the curing bath, were as outlined in detail, following:

(1) The water bath of the consistometer was filled, leaving space for rise of the water level when the can was inserted.

(2) About 5 grams of sodium dichromate crystals were added to inhibit rusting and corrosion of metal parts that operated in the bath.

(3) A thin film of lubricating oil was dropped on the bath-water surface to reduce evaporation.

(4) The calrod heater switch was turned on.

(5) The electric motor was connected to drive the water pump.

(6) The thermo-regulator was positioned to maintain approximately the required bath temperature, 140°F.

(7) A thin film of lubricating oil was applied to the inside of the can so that the cement would not stick when it thickened, and the can was placed in the water bath.

(8) 6.345 grams of quebracho extract were weighed out and placed in a clean Erlenmeyer flask.

(9) When the bath reached approximately 140°F the thermo-regulator was adjusted until the temperature was continuously maintained at 140 ± 0.5°F.

(10) When the temperature was steady, 3100 grams of dry, sieved cement were weighed out and placed in the enamel pan.

(11) Distilled water was siphoned from the storage bottle and 1240 grams were weighed out in the mixing vessel.

(12) The quebracho was added to the mixing water after first being dissolved in the Erlenmeyer flask. The flask was carefully rinsed with some of the distilled water and the wash water was transferred to the mixing vessel to assure the inclusion of all the quebracho.

(13) Then the cement was quickly added to the water with a large spoon, meanwhile mixing with a slow-speed electric stirrer. As soon as the cement was all initially wetted the agitation was continued for 2 minutes with a high speed stirrer. The total mixing time from the first addition of dry cement until the slurry was placed in the can did not exceed 5 minutes. This agrees with the specification of API Code 32, which allows a maximum of 5 minutes for these operations.

(14) The slurry was then added to the can, to the prescribed level, 1 inch from the top.

(15) The stirrer and lid assembly were quickly placed on the can and screwed into place, the stirrer having been coated lightly with lubricating oil.

(16) The worm was engaged with the can-lid worm gear and its positioning pins and screws were tightened into place.

(17) The stirrer motor and the electric timer were started, signalling the beginning of the run.

(18) As soon as any preliminary fluctuation of the moment arm had ceased the consistency was read and recorded.

(19) Readings were taken at succeeding 10-minutes intervals for the first hour, or at increments of 10 poises, whichever was the sooner. After one hour readings were taken only at 30-minute intervals, or at increments of 10 poises, whichever was the sooner.

(20) The run was stopped when the consistency reached 70 poises and the time was recorded, giving the length of the run as 6.233 hours.

(21) The can was opened and the cement was removed to the molds as quickly as possible.

(22) The molds were then immersed in the curing bath at the same temperature as the test, 140°F.

When the cement was removed from the consistometer can it was placed in two, 6-cube steel molds. These molds were as shown in Figure 11. When cured, the hardened cement cubes were removed from the molds and crushed on the hydraulic compression tester to determine the total compressive strength, from which the unit compressive strength was calculated, as shown in Appendix D. The total experimental procedure for all steps was as outlined below:

(1) The curing-bath container was filled with water and the calrod heater was switched on.

(2) The thermo-regulator was set to control at approximately

the test temperature of 140°F.

(3) The cement molds were cleaned and the inside surfaces were brushed with a solution of 6% paraffin in carbon tetrachloride. This prevented the cement from sticking to the mold when it was removed after hardening.

(4) When the temperature came up to approximately 140°F in the bath the stirrer was started and the thermo-regulator was adjusted to maintain carefully that temperature, ± 0.3°F.

(5) When the cement was removed from the consistometer can it was poured into each mold compartment, filling each one half-way.

(6) Using a short glass rod, each of the compartments was puddled to mix the cement evenly and remove any lumps. The puddling stroke was repeated 24 times in each compartment and then the molds were filled to overflowing.

(7) With a smooth-edged spatula the excess cement was scraped off, leaving a flat surface flush with the top of the mold.

(8) A smooth, greased, glass cover plate was pressed over the top of each mold to prevent water from disturbing the cement as it hardens.

(9) The molds were then immersed on the racks in the curing bath and the lid was closed. The time of insertion was recorded.

(10) When the molds had been in the bath for 23¼ hours they were removed and opened. The cubes were then placed in a bucket, or other suitable vessel, which served as a cooling bath. It contained water at the test temperature of 140°F.

(11) The cubes were slowly cooled, the cooling rate being adjusted by a small incoming stream of cold water. This cooled the cubes to a temperature of 80 ± 5°F in 35 ± 5 minutes, after which they remained at this temperature until tested in compression.

(12) The cubes were then carried immediately to the compression tester to be crushed.

(13) Each cube, in turn, was dried, placed centrally on the lower platen and elevated into place against the upper platen.

(14) The hydraulic oil pump was started and the pulling head was raised by the hydraulic cylinder, so that it was loading at a rate of 4,000 lbs./minute.[18]

(15) The pump was kept driving at this rate until the cube suddenly fractured. At that instant the pointer on the pressure dial indicated the maximum load sustained by the cube.

(16) As soon as the cube was thus fractured it was removed

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[18] Am. Soc. Testing Materials, Standards. Part II, 81, (1944).

and replaced by another, and the procedure was repeated until all the cubes had been tested.

CHAPTER IX

RESULTS AND DISCUSSION

The first seven runs were made using plain, Type I Portland cement and distilled water, while the last five were made with special additions of chemicals to the mixing water, in order to try to produce a retarded set.

Consistency Tests

Runs No. 1 and 2 were made at a 100°F test temperature with plain cement and water and the results are recorded in tabular form in Tables XIV and XV, and in graphic form in Figure 14. All the test points were plotted and the best average curve was drawn, shown as the solid line.

All other consistency data have been plotted in this manner, i.e., the data for all runs at any one temperature were plotted on one graph and an average curve was drawn through the points.

It may be seen from Figure 14, that the rate at which the cement thickens is an expontential function of time, increasing more rapidly as the time of test increases. Also shown on Figure 14, as a dotted line, are the averaged

results obtained by the manufacturer* of the cement, using the Halliburton Consistometer. It is evident that, while the general shape of the curves are similar, the rate of stiffening of the cement, which was obtained in this investigation, is greater over the whole range than the rate reported by the manufacturer.

Runs No. 3, 4, 5 and 7 were made at 140°F and the test results are shown in Tables XVII, XVIII, XIX and XXIV. The data for Run No. 3 are few, since there was a breakdown in the equipment during the run. An attempt was made to relieve a binding that developed in the bearing pivot on the can and, in so doing, the revolving can was jammed, causing it to disengage the gears and break the cord to the consistency quadrant scale. Repari of the damage necessitated a shutdown of the equipment and the cement was discarded since it had not been stirred long enough to reach the proper consistency for molding. The data from Run No. 3 were omitted from the graphic results because they were incomplete, but Figure 15 shows the data plotted from Runs No. 4, 5 and 7, with the average curve drawn as a solid line. The dotted line represents the data furnished by the manufacturer** of the cement, for similar tests at 140°F.

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*Obtained by personal communication with Mr. James M. Adams of the Waco, Texas, office of the Universal Atlas Cement Company.

**Ibid.

Run No. 6 was made at 180°F, this being chosen as the highest test temperature, since it equals the usual top temperature used for commercial consistometer tests at atmospheric pressure. The data of Run No. 6 are given in Table XXI and they are plotted on Figure 16 as a solid line, The dotted line represents the data of Farris[19] for similar tests on plain Portland cement at 180°F. Figure 17 is a combination of the data of Figure 14, 15 and 16, plotted on a common scale to allow more convenient comparison of the effects of temperature upon consistency. It can be seen from Figure 17 that both the consistency and the rate of change of consistency with respect to time increase with temperature. Since the limit of mobility is the most important criterion upon which the experimental results may be judged, the effect of test temperature upon the limit of mobility is shown in Figure 18.

After Run No. 1 the consistency was not allowed to reach 100 poises while the cement was still being stirred. It was found that the cement at the ends of the stirrer blades stuck to the wall of the can if it was allowed to stiffen to such a consistency, since the cement at that time was approaching its initial set. For this reason, the cement that stuck was extremely hard to remove after sitting

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[19]Farris, op. cit., p. 121.

in the can for the few minutes required to remove the lid and pack the compression molds full of the fluid cement and place them in the curing bath. The total elapsed time was usually about 10 minutes for these operations and removal of the stiff cement that remained in the can required the use of a long copper-tube gouging tool, so chosen as not to score the inside of the harder brass can. In subsequent runs the stirring was stopped when the consistency reached about 85 poises, although in a few instances the runs were carried on longer.

In industrial practice when the consistency of any slurry reaches 70-80 poises the test is usually stopped and the cement removed immediately from the can. This may be necessary when the rate of setting is rapid, as in the case at higher temperatures. When tests are stopped before the consistency reaches 100 poises the data are plotted and the curve should be extrapolated to 100 poises.

The results of the experimental works carried out in this investigation on plain Portland cement show higher rates of setting, throughout the whole range covered by the tests, than are reported by either Farris[20] or the manufacturer of cement. The difference between the results of this study and those of the manufacturer may be explained, partially at

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[20]Farris, op. cit., p. 121.

least, by the difference in the rates of rotation of the consistometers, since the equipment used in both cases was similar in all other respects. The manufacturer used the Halliburton machine which rotated at about 25 r.p.m. and the consistometer built for this investigation rotated at 43.8 r.p.m.

The data given by Farris[21] show lower rates of setting than those reported by the manufacturer, which, as stated above, are lower than the rates obtained in this investigation. Farris' consistometer rotated at 47 r.p.m., roughly the same speed as that of the experimental consistometer, therefore, the setting rates of Farris' work should compare with the rate of this investigation and should be higher than those of the manufacturer. Farris, in his article, gave no details of the construction of his apparatus, nor of the brand of cemant which he used, so it is possible to state exactly why his results are not in closer agreement with those of this study, other than that the properties of the Portland cement may have been different.

The first test with a chemical retardant was Run No. 8, using $Na_4P_2O_7 \cdot 10H_2O$ at 140°F. The data are given in Table XXVI and the graphic results are shown on Figure 20. Contrary to expectations, the sodium pyrophosphate did not retard thesetting, rather it increased the rate. For this

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[21] Farris, op. cit., p.121.

reason, no further tests on the addition of sodium pyrophosphate were made.

The next chemical additive was quebracho. Four runs were made at varying concentrations of additive, all at 140°F, and the experimental data are given in Tables XXVII, XXVIII, XXIX and XXXII. In every case the stirring time was greater than for plain Portland cement at 140°F. The results are shown in graphic form on Figures 21, 22, 23 and 24. The range of concentrations tested was 0.051 to 0.205% quebracho by weight of dry cement. The limit of mobility was increased over that measured for plain Portland cement by 0.449 to 1.076 hours. In every case the increase in quebracho concentration increased the total stiffening time. The limit of mobility at 0.154% quebracho was greater than that at 0.205% quebracho by about 0.07 hours. However, the limit of mobility first increased, reached a maximum (at 0.154% quebracho), and then decreased with increasing quebracho concentration in the slurry. This phenomenon can be seen on Figure 25.

The stirring time results obtained in all the quebracho-retarded runs compare favorably with tests made on commer-slow-setting cements, as shown in the following table.

TABLE III

TIME IN HOURS FOR 40% SLURRIES
TO REACH A CONSISTENCY OF 100 POISES

Investigator	Cement Used	100°F	140°F	180°F
Farris[22]	Oil-well cement "C".	5.2*		
	Oil-well cement "B"			3.7*
Neighbors and Cromer[23]	Slow-set cement "A"		3.08	
	Slow-set cement "B"		4.0	
This investigation	Universal Atlas Portland (quebracho retarded)	8.0*		

A noticeable effect of increasing quebracho concentrations is the greater time required to reach the point at which the rate ofsetting begins to show a rapid increase, as depicted on Figures 21-24.

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[22]Farris, op. cit., p. 121, 126.

[23]Neighbors and Cromer, op. cit., p.3.

*Extrapolated from 80 poises.

Theconsistency curve for Run No. 10, as shown on Figure 22, is typical of the general shape which is desired for consistency curves of retarded cements. It starts out with a slight positive slope, increases in slope at an even rate of acceleration, and then results in a nearly vertical slope at 100 poises. However, greater concentrations change the shape of the curve as shown on Figures 21, 23 and 24 for Runs No. 9, 11 and 12. At the start these curves take the usual positive slope, but there follows a short period of decceleration, after which the slope actually can become negative, as in the case of Run No. 9. Then the slurry begins the usual upward trend of thickening and follows the general course. No explanation can be offered for this occurence.

There is one other peculiarity of these runs with quebracho and it is best illustrated on Figure 21 for Run No. 9, where the highest concentration (0.205%) of quebracho was used. Reference is made to the sudden drops in consistency which were followed by slow rises to the same level of consistency as before the drops. At such times in the test runs the consistometer actually revolved much easier for a few minutes, gradually climbing back to the higher readings.

It is felt that the fluctuating consistencies recorded near the ends of Runs No. 9 and 12 were caused by

a condition similar to the one reported by Farris[24], which he describes as "plug-type flow." In this case the slurry began stirring uniformly, but as it stiffened it became more and more difficult for it to pass through the restrictions of the stirrer blades. This caused the cement to stick to the blades and the whole core of cement around the shaft then whirled as a plug. In so doing it was only shearing at the wall of the can and the water in the slurry was serving to lubricate this slippage. Hence, the sudden drops to a lower consistency which gradually built up to the normal value. Then, after a short period of normal progression of setting, the same phenomenon occurred. It will be noted on Figure 21 that the point at 4.02 hours was neglected in plotting the curve. This reading was abnormally high, but as it lasted for only a few seconds it was thought to be due to temporary presence of some cement grains thrown into the stirrer bushing, and that it had no significance otherwise.

The existence plug-type flow is a reasonable conclusion in the light of the fact cited by Farris[25] that all the cements he tested showed the very undesirable characteristics of free-water separation, with the exception of standard Portland cement. This explains the possibility of the presence

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[24]Farris, op. cit., p.125.

[25]Ibid., p. 127.

of the water which accumulates and allows the stiffening plug to whirl so easily. Possibly this leaves a dehydrated slurry in the core which might stiffen more rapidly than the other slurry, explaining the mechanism of formation of the stiff plug.

The strong possibility that such a condition existed in this investigation was evidenced by the presence of several fluid ounces of free water on top of the thickened slurry in the can at the end of the run. Thus it appears that this cement, and many tested by other investigators, are retarded at the expense of one other desirable quality. If a cement could be retarded so that it would retain all the desirable qualities of Portland cement, it is very likely that the tendency toward plug-type flow would be greatly reduced.

Compression Tests

As mentioned in the introduction, the resultant compressive strength developed by the hardened cement is an important factor to be considered in the choice of an oil-well cement. The results of the compressive strength tests on plain Portland cement are given in Tables XVI, XX, XXI, XXIII and XXV, and are shown graphically on Figure 19. It is immediately apparent that the strength of set cement

after 24 hours is increased as the curing temperature increases. In fact, the strength of the plain Portland cement tested was nearly twice as great for 180°F as it was for 100°F, the actual value being 4522 psi as compared to 2454 psi. This compares faiely with the data supplied by the manufacturer of the cement, wherein the strength values reported for 40% slurries, cured for 24 hours at 100° and 140°F, respectively, are 3060 and 6325 psi.

It will be noted in Table XX that the strength of the cement in Test Run No. 4 was inordinately high. The cubes were cured in the standard manner, but at the time of the compression tests trouble was experienced with the compression tester and the pressure developed by the machine was insufficient to break the cement. This condition was remedied on the following day and when the cubes were finally crushed, they had been cured for a total of 41 hours, the last 18 hours being at a temperature of 80° F. The average compressive strength developed at 41 hours was 6163 psi. This value compares more closely to the manufacturer's value of 6325 psi at 24 hours, indicating that, although the cement did not strengthen as fast as specified by the manufacturer, it was probably just as effective and would finally reach approximately the same ultimate strength expected from a fresh sample of the same cement.

The results obtained from the compressive strength

tests on the retardant-treated slurries are given in Tables XXVII, XXXI, XXXII, XXXIV and XXXV. The strength of the set cement was diminished by the addition of sodium pyrophosphate, the average strength being 3757 psi at 140°F, as compared to 4249 psi for plain Portland cement at 140°F. This would be expected, according to the data of the manufacturer, wherein the test results were as follows:

TABLE IV

COMPRESSIVE STRENGTHS FOR 40% SLURRIES CURED AT 140°F

(Universal Atlas Cement Company)

Type Cement Used	Psi	
	Cured 24 hrs.	Cured 3 days
Type I plain Portland cement	6325	8000
Retarded-set oil-well cement	2900	6160

Obviously, one would expect lower strengths from slurries containing chemical retarding additives and the effect seems to hold true over a period of many days.

The addition ofquebracho greatly improved the early strength of the hardened cement, as seen on Figure 26. The average increase was 28.8% over the compressive strength of plain Portland cement at 140°F. Such increases in strength were evidenced at all concentrations of quebracho used, but

there was no exact relation between the amount of reagent used and the strength developed in the set cement. The general trend is toward increasing strengths with increasing concentrations, in the range tested. But the greatest strength occurred at a concentration of 0.15%, so it could be postulated that quebracho probably is the best to be used in a concentration range of 0.15-0.20% for the optimum compressive strength at 140°F.

When the cement cubes were removed from the molds they often had structural faults, such as low spots, fissures and holes on the surface, and bubbles of air trapped on the inside, the latter being found after the cubes had been crushed. By more careful puddling in the latter tests performed the larger bubbles were practically eliminated when the cement was added to the molds. There is some possibility that the high-speed agitation applied to the slurry at the time of mixing served to introduce air into the slurry, although care was taken not to let the stirrer blades come above the surface of the liquid slurry while it was being mixed. But some scheme should be devised to preclude the formation of pinhole bubbles that were observed throughout the structure of the hardened cement. Some defoaming agent, such as tributyl phosphate, added to the mixing water in small quantities, might decrease this retention of air.

It is not known why the experimental values of compressive strength for plain Portland cement were consistently lower than those supplied by the manufacturer, but it is possible that the previous history of the cement may account for this fact. That is, if the cement were stored in a moist atmosphere and had absorbed some moisture, the subsequent strength would be reduced. However, the test samples were stored in air-tight containers as soon as they reached the experimental laboratory.

The results obtained in compressive tests of the quebracho-retarded cement were unique, and they are a significant contribution to the knowledge of the subject, since other such retardants ahve lowered the strength of the set cement. No tests were made at temperatures above 140°F, using quebracho, therefore, there is no certainty that it will react favorably at higher temperatures. However, further investigations seem to be in order, particularly as an attempt to obtain a definite correlation between the amount of quebracho added and the resultant compressive strength of the set cement.

CHAPTER X

CONCLUSIONS

From the experimental work carried out in this investigation the following conclusions can be drawn:

(1) Sodium pyrophosphate decahydrate increased the setting rate and decreased the compressive strength of Portland cement after 24 hours, therefore, it should never be used as an additive for retarded cements.

(2) Quebracho in amounts from 0.051% to 0.205% by weight of dry cement used decreased the setting markedly and and extended the limit of mobility. These results compare favorably with those of tests on commercial retarded cements.

(3) Quebracho in the amounts mentioned under (2) increased the compressive strength of the plain Portland cement used. There was found no record in the literature of any retardant which had, heretofore, increased the strength of the set cement.

BIBLIOGRAPHY

BIBLIOGRAPHY

American Society for Testing Materials, Standards. Part II. Nonmetallic Materials - Constructional, 1, Philadelphia, (1946).

Ibid., pp. 1, 25, 81, (1944).

Ibid., p. 18, (1939).

Anon., "Pipe - National's Anthem," Esso Oilways 16, No. 10, 1, (1950).

API Code 32 for Testing Cements Used In Wells, American Petroleum Institute, First Edition, 5, New York, (1948).

Bogue, R. H. and Lerch, W., Research Reports, Portland Cement Association Fellowship at the National Bureau of Standards, Sept., 1933.

Budnikov, P. P., Kukolev, G. V. and Leshoev, V. M., Chemical Abstracts 23, 5293, (1929).

Davis, E. L., California Oil World 31, No. 13, 14, (1938).

Desch, C. H., Chemical Abstracts 24, 1952, (1930).

Farris, R. F., "Effects of Temperature and Pressure on Rheological Properties of Cement Slurries," American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1207 (Petroleum Development and Technology) 142, pp. 119, 121, 123-27, (1941).

Garre, B., Chemical Abstracts 22, 149, (1928).

Gordon, G. M., Chemical Abstracts 24, 3339, (1930).

Koyanagi, K., "By-product Gypsum As A Retarder," Rock Products 35, No. 2, 36, (1932).

Ludwig, N. C., "Portland Cements in the Oil Industry," The Oil and Gas Journal 46, No. 14, 105, (1947).

Machinskii, E. K., Chemical Abstracts 35, 1595, (1941).

Neighbors, G. R. and Cromer, S., "Some Factors Controlling the Pumping Time of Oil-Well Cements," American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1399 (Petroleum Technology) 4, No. 6, pp. 3, 5, (1941).

Pershke, V. K., Chemical Abstracts 26, 4433, (1932).

Petroleum Facts and Figures, American Petroleum Institute 6th Edition, p.68, (1939).

Petroleum Facts and Figures, American Petroleum Institute 8th Edition, p. 89, (1947).

Research Reports, Portland Cement Association of the United States of America, p. 3, New York, April, 1941.

U. S. Minerals Yearbook for 1944, p. 1230, Washington, D. C., (1946).

Weiler, J. E., The Petroleum Engineer 9, No. 12, 33-4, (1938).

Work, L. T. and Lasseter, F. P., Chemical Abstracts 25, 4375, (1931).

Yamane, S., Chemical Abstracts 42, 2075, (1948).

Zehmen, H. A., Journal of the American Concrete Institute (Abstracts) 3, 51, (1932).

APPENDICES

APPENDIX A

STUDY OF THE LITERATURE ON ADDITIVES

In 1927, Garre[26], of Germany, noted that as little as 0.001% of lead oxide, PbO, delayed the hardening process of cement, the effect increasing with additional amounts. Three Russian investigators, Budnikov, Kukolev and Leshoev[27], gave test results showing that a cement slurry with a Na_2SiO_3 concentration of 0.01 normality was as fluid with 42.5% water as the same slurry, untreated, was with 48% water. They also reported that Na_2CO_3 and NaOH were less effective for the same purpose. Desch[28], of England, found that the addition of Zn and ZnO increased the period of initial set but lowered the strength of the Portland cement tested.

An interesting study by an American investigator, Gordon[29], brought results closely related to the problem of set-retardants. He made 1000 tests on oil-well cements and determined that the strength of a cement is highest when the

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[26] Garre, B., C. A. 22, 149, (1928).

[27] Budnikov, P. P., Kukolev, G. V., and Leshoev, V. M., C. A. 23, 5293, (1929).

[28] Desch, C. H., C. A. 24, 1952, (1930).

[29] Gordon, G. M., C. A. 24, 3339, (1930).

minimum amount of mixing water is used. This also held true when cements were mixed with $CaCl_2$ solutions instead of water.

In another rather broad category, Work and Lasseter[30], determined that hydroxides react as initial set-retardants. Koyanagi,[31] a well-known Japanese experimenter, stated that test results showed P_2O_5-water solutions to be a retarding group with little effect on the strength of the set cement. In Germany, Pershke[32], made experiments on cement, using water, KCl solution, NaCl solution, and $MgCl_2$. The NaCl was added in powder form before the mixing water, but it resulted in an acceleration of setting. KCl did not affect the accelerating action of the NaCl solution and $MgCl_2$ was found to delay the setting. Higher temperatures caused the setting process to begin sooner but increased its duration.

Zehmen[33] noted that crystallization and hardening could be retarded by adding substances that would coagulate the hydrosols of SiO_2, Al_2O_3 and Fe and transform them into gels. He found that sugar (sucrose), calcium sucrate, copper chloride and lead nitrate all act as retarders. In 1940,

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[30]Work, L. T. and Lasseter, F. P., C. A. 25, 4375, (1931).

[31]Koyanagi, K., Rock Products 35, No. 2, 36, (1932).

[32]Pershke, V. K., C. A. 26, 4433, (1932).

[33]Zehmen, H. A., J. Am. Conc. Inst. (Abstracts) 3, 51, (1932).

the Russian, E. K. Machinskii[34], reported on what he called "mixed cements for oil wells." His specific results showed that borax and sulfite cellulose extract are good retarders and strength developers when used in oil-well cements containing hematite, that being one of the iron ores, mostly Fe_2O_3.

Yamane[35], another Japanese investigator, gave some qualitative results on four kinds of Portland cement which he mixed in 10-gram quantities with 10 cc. of dilute $CaCl_2$ solution. In each case there was a preliminary sharp rise in consistency, followed by an immediate drop. The time required for setting was directly proportional to the amount of SO_3 in the cement as $CaSO_4$, this material being added by the manufacturer as a retardant. The setting seemed to occur only when all the $SO_4^=$ ion had disappeared from the slurry by chemical reaction.

Patented Retardants

U. S. 2,471,632

This patent relates to the use of NO_2-oxidized cellulose and inorganic salts of this oxidized cellulose as retardants for Type II Portland cement. (OC shall be an

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[34]Machinskii, E. K., C. A. 35, 1595, (1941).

[35]Yamane, S., C. A. 42, 2075, (1948).

abbreviation meaning: oxidized cellulose)

When mixed rapidly, OC and its inorganic salts act as foam-stabilizing agents and cause air-entrainment, which weakens the structure of the cement as it sets. This effect was nullified by the use of tributyl phosphate as a defoaming agent. It was added in amounts of 0.02% by weight of dry cement.

Strength tests were made on compression cubes cured in water baths at 140°F and 200°F for 24 hours and for 3 days and they showed that the retardants had little effect on the strength.

The OC was added to the cement powder in dry form and mixed by hand, but the salts were added to the slurry mixing water in solution form. However, they may be added in either way. The amounts of retardants added are given as percentage by weight of dry cement used. The tabulated results of the investigator's experiments are shown below:

TABLE V

HOURS REQUIRED FOR SLURRY CONSISTENCIES TO REACH 100 POISES

Retardant %	140°F	180°F	200°F	220°F
None	3.40	1.83	1.55	1.20
OC - .09	13.10	13.50	6.78	2.02
OC - .06	7.90			
OC - .03	3.97			

TABLE V (continued)

Retardant %	140°F	180°F	200°F	220°F
OC - .27				3.68
OC - .21				3.12
OC - .15				3.60
K(OC) - .10			4.52	
K(OC) - .075			4.12	
K(OC) - .05			3.80	
NH_4(OC) - .10			5.88	
NH_4(OC) - .075			4.95	
NH_4(OC) - .05			4.28	

The results of the tests on compressive strength are shown in the following table:

TABLE VI

COMPRESSIVE STRENGTHS AT TIMES INDICATED
(PSI)

Retardant %	Cured at 140°F		Cured at 200°F	
	24 hrs.	3 days	24 hrs.	3 days
None	2,843	4,879	4,140	4,712
OC - .09	3,073	3,800	3,800	4,954

U. S. 2,470,505

This patent relates to the use of maleic acid and modified starch as retardants for Portland cement. The preferred starches are those known, commercially, as thin-boiling starches, but oxidized starches may be used. The degree of solubility of such starches varies, but ones with a solubility of 50-65% are best. The maleic acid used was technical grade.

The starches of lesser solubility tend to be more reactive at temperatures above 140°F and as high as 200°F and no starch will give equal stiffening times at all temperatures. The table shown below is a result of consistometer tests by the investigator and the percentages of retardants are given by weight of dry cement.

TABLE VII

TIME FOR 40% SLURRIES TO REACH CONSISTENCY OF 100 POISES (HOURS)

Retardant	%	100°F	140°F	180°F	200°F	220°F
None		6.70	3.00	2.02	1.78	1.53
Maleic acid	0.10	8.77	3.30	2.63	3.50	2.12
Maleic acid	0.20	9.40	3.90	3.15	7.13	3.32
Maleic acid	0.30	11.92	4.78	4.17	10.13	4.87
Mod. Starch	0.10	7.80	6.62	7.92	5.45	2.57
Mod. Starch	0.12	8.75	9.03	10.08	6.72	2.80
Mod. Starch and Maleic acid	0.06 and 0.10		5.17	5.67	5.87	3.25

The density and the compressive strength of the cement were practically unchanged at the time of initial set and the results of the compressive strength tests are given in the following table:

TABLE VIII

COMPRESSIVE STRENGTHS AT 180°F CURING TEMPERATURE

(PSI)

Retardant	%	24 hrs.	3 days	7 days
None		5,158	7,300	6,929
Maleic Acid	0.30	5,025	6,504	6,829
Mod. Starch	0.10	4,597	9,417	10,710
Maleic Acid and Mod. Starch	0.10 0.06	5,179	7,329	8,625

U. S. 2,429,211

This patent relates to the use of a starch modified by an oxidant or hydrolyzer as a retardant for Portland cement. The modified starch composition is formed as finely divided particles which are not more than 60-65% soluble in water. These particles disperse, some going into solution, and form practically no gel or thickened material.

Some of the oxidizing agents used were (1) calcium hypochlorite as a 5% solution to digest the starch for 5

days at room temperature, (2) 1% solution of sodium peroxide, digesting at 102°F for 24 hours, and (3) 0.3% hydrogen peroxide solution, digesting for 1 hour at 140°F. One also could use water, made 0.25% N with hydrochloric acid or ammonium persulfate in the presence of peracetic acid, so that hydrolysis and oxidation take place either simultaneously or, probably, in succession, the end product following the products resulting from hydrolysis.

Raw corn starch was the base material and the modified starch was added in amounts given as percentage by weight of dry cement. It is best to employ a modified starch that begins to dissolve at 140°F, the essential fact being that the starch exerts its most effective action above some minimum temperature which corresponds roughly with the point at which it begins to dissolve.

The following table gives the results of the experiments performed by the inventor.

TABLE IX

TIME REQUIRED FOR SLURRY TO REACH LIMIT OF MOBILITY (30POISES) AT GIVEN TEMPERATURE

Retardant %	Starch Solubility (80°F)	Time in Hours				
		100°F	140°F	180°F	200°F	220°F
None		6.33	3.00	2.25	2.00	1.75
.15 - .20	Up to 10%	6.75	3.25	6.50	6.00	3.50
.12 - .15	10 to 25%	8.00	7.00	7.50	5.75	2.83
.10 - .12	25 to 40%	9.75	10.25	8.50	5.50	2.33
.08 - .10	40 to 65%	16.00	10.45	7.00	5.25	2.00

U. S. 2,427,683

This patent relates to the use of carboxy-methyl-cellulose (CMC) and its metal salts (Na, K, Al, Cu, and Fe), or hydroxy-ethyl-cellulose (HEC) as setting retardants. Additions of 0.05-0.75 lbs. of CMC per 100 lbs. of dry cement retard the setting time at 180-220°F by 3 to 10 hours. Additions of 0.05-0.50 lbs. of HEC per 100 lbs. of dry cement retard the setting time similarly, but in the 140-180°F temperature range. It is ordinarily preferred to use CMC and its salts, either alone or in combination, so that the total of such additives lies within the range of 0.05-0.64%. When CMC and HEC are used together the cement has a fairly uniform setting time, in the order of 5 hours, over a range of 140-220°F.

The CMC and its salts can be added to the dry cement in powder form and intermixed before addition to the slurry or they can be added to the slurry in solution. It is best, commercially, to employ CMC and its water-soluble salts and add the material to the dry cement. In the test results shown on following pages, this was the procedure for addition except where otherwise noted.

In cement slurries, when mixed rapidly, the CMC and its salts act as foam stabilizers and cause air entrainment. This results in excessive frothing and foaming, so it must be nullified by the use of a defoamant. Tributyl phosphate

and pine oil, in quantities of 0.02-0,05% were found to be successful defoamants, and in each slurry tested, which contained CMC and its salts, 0.02% tributyl phosphate was used.

The following tables give the results of tests described in the patent.

TABLE X

TIME REQUIRED TO REACH CONSISTENCY OF 80 POISES AT CONSTANT TEMPERATURES

Cement	Additives and % Used	Stiffening Time in Hours			
		140°F	180°F	200°F	220°F
Type I	None	2.15	2.20	0.70	0.53
Type I	Na-CMC 0.24	2.88	3.60	5.35	6.96
Type II	None	3.76	1.78	1.48	1.18
Type II	Na-CMC 0.16	3.55	2.96	5.61	10.65
Type II	Na-CMC 0.32	3.75			
Type II	Na-CMC 0.64	4.96			
Type II	0.06 Na-CMC + 0.125 HEC	6.46	5.26	5.18	3.76
Type II	0.08 Na-CMC + 0.125 HEC	6.33	5.67	6.55	5.20

TABLE XI

COMPRESSIVE STRENGTH OF HARDENED CEMENT

Cement	Additive And % Used	Psi at age indicated			
		Cure at 140°F		Cure at 200°F	
		24 hrs	3 days	24 hrs	3 days
Type I	None	4093	5780	3063	3327
Type I	Na-CMC 0.24	3107	5733	3925	4900
Type II	None	2437	4860	4269	4625
Type II	Na-CMC 0.16	2423	5227	3450	6230
Type II	0.08 Na-CMC + 0.125 HEC	3783	6230	5027	6180

TABLE XII

TIME REQUIRED TO REACH CONSISTENCY OF 80 POISES AT 200°F

Cement	Additive and % Used	Stiffening Time in Hours
Type II	None	1.48
Type II	Na-CMC 0.16 (powder)	5.61
Type II	CMC 0.15 (powder)	3.00
Type II	CMC 0.30 (powder)	7.10
Type II	K-CMC 0.075 (solution)	3.90
Type II	K-CMC 0.15 (solution)	8.68
Type II	NH_4-CMC 0.15 (solution)	3.35
Type II	NH_4^+-CMC 0.30 (solution)	9.12
Type II	Al-CMC 0.15 (powder)	2.68
Type II	Al-CMC 0.30 (powder)	4.83
Type II	Cu-CMC 0.50 (powder)	2.25
Type II	Cu-CMC 0.75 (powder)	2.46
Type II	Fe-CMC 0.50 (powder)	3.55
Type II	Fe-CMC 0.75 (powder)	4.98

The two cements used for these tests had the following analyses:

TABLE XIII

CEMENT ANALYSIS

Cement	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	SO_3	Ign.Loss
Type I	21.8	6.0	2.5	65.0	1.1	0.16	1.70	1.20
Type II	22.1	4.8	4.3	64.2	0.88	0.20	1.70	1.20

U. S. 2,374,628

The inventor states that admixtures of dextrins, starches or grain and vegetable flour up to 0.1 % retard the setting of cement up to about 200°F.

U. S. 2,374,581

The inventor states that admixtures of $NaHCO_3$ and/or tartrates of 0.01-1.00 % retard the setting of Portland cement at temperatures up to 200°F in deep wells.

U. S. 2,307,485

This patent claims that about 0.005 % of a sulfonated amino-hydroxy triphenyl methane dye, such as "Patent Blue A", improves the plasticity of Portland cement.

U. S. 2,290,956

This patent relates to the use of 0.2-0.4 %, by weight, of casein to retard the setting rate at high well temperatures.

U. S. 2,233,974

This patent relates to the use of about 0.01-1.0 % of an alkali metal triphosphate to retard setting time.

U. S. 2,233,973

This patent relates to the similar use of an alkali metal hexametaphosphate.

U. S. 2,211,368

This patent relates to the use of a retardant of the following composition:

Boric acid	52.5 %
Borax	26.2
Gum arabic	5.2
Calcium tartrate	12.6
Tartaric acid	3.5

It is claimed that the tartaric acid neutralizes the alkali in the cement, the calcium tartarate serving to produce a uniform setting time between 140-180°F.

U. S. 2,188,767

This patent relates to the use a solution of caustic alkali and a material of the class consisting of humic, gallic, tannic, quercitannic or lignic acid. This retardant, when admixed with Portland cement, makes a material that is suitable for cementing oil wells.

U. S. 2,085,044

The inventor claims a slow-setting cement can be made by heating Portland cement to 105-130°C and treating it for more than 5 minutes with superheated steam at a temperature of 105-130°C.

U. S. 2,006,426

This patent relates to the use of a retardant consisting of some water-soluble boron compound, such as sodium

borate or boric acid, and a water-soluble gum, such as gum arabic. When this is mixed with a Portland cement it forms a fluid hydraulic cement slurry, suitable for oil-well use.

U. S. 1,852,595

This patent relates to the use of calcium borate or calcium oxychloride as a retardant for Portland cement that is to be used in oil wells.

Britain 502,015

This patent relates to the use of a mixture of an aqueous solution of an alkali metal hydroxide and tannin, or a tannin derivative, as a cement-setting retardant. If added in sufficient quantity it is said to retard the initial set and reduce the viscosity of the slurry.

Britain 294,111

The inventor describes a slow-setting cement that develops high initial strength, made by increasing the alumina content of a Portland cement and adding a protective colloid such as albumen, casein, gelatin, gum, algae or starch. Bauxite may be added to the raw materials or calcic aluminate may be added to the clinker before or after grinding, and the colloid may be added dry or with the gaging water. An illustrative sample composition is:

1000 parts cement
200 parts calcic aluminate
4-8 parts casein.

These are to be mixed dry and then gaged with water.

Germany 595,924

The inventor states that the setting of a hydraulic cement is delayed by the addition of size or size-forming agents. He used a mixture of potato meal and NaOH, however, sulfite waste lye can also be used for the caustic.

APPENDIX B

TABLES OF EXPERIMENTAL DATA

TABLES XIV AND XV

SLURRY CONSISTENCIES FOR RUNS NO. 1 AND 2 AT 100°F

RUN NO. 1	
Time From Start Of Run, Hours	Consistency In Poises
0	
.067	25
.167	24
.375	26
.533	27
.666	30
.833	35
1.017	42
1.167	43
1.333	45
1.967	84
2.067	100

RUN NO. 2	
Time From Start Of Run, Hours	Consistency In Poises
0	25
.483	27
.683	30
.850	32
1.083	40
1.618	51
1.750	65
1.918	75
2.000	80

These runs were made with a 40% slurry, using 3000 grams of Type I Portland cement and 1200 grams of distilled water.

TABLE XVI

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 2

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	9,640		4.00	2,410
2	11,500		4.00	2,875
3	8,740		4.00	2,185
4	10,940		4.00	2,735
5	9,480	0.19	3.81	2,488
6	9,880		4.00	2,470
7	9,960		4.00	2,490
8	8,000		4.00	2,000
9	9,640		4.00	2,410
10	10,320		4.00	2,580
11	9,480		4.00	2,370
12	9,640		4.00	2,410

Average compressive strength of all values = 2452 psi

Allowable deviation = ± 245 psi

Allowable limits are 2207 - 2697 psi

True average compressive strength = 2454 psi

TABLE XVII

SLURRY CONSISTENCIES FOR RUN NO. 3 AT 140°F

Time From Start of Run, Hours	Consistency In Poises
0	25
.167	26
.333	26
.500	33
.667	41
Breakdown	

This run was made with a 40% slurry, using 3100 grams of Type I Portland cement and 1240 grams of distilled water.

TABLES XVIII AND XIX

SLURRY CONSISTENCIES FOR RUNS NO. 4 AND 5 AT 140°F

RUN NO. 4		RUN NO. 5	
Time From Start Of Run, Hours	Consistency In Poises	Time From Start Of Run, Hours	Consistency In Poises
0	28	0	28
.167	31	.159	29
.333	33	.325	32
.500	40	.492	35
.667	46	.675	48
.833	55	.775	56
.917	75	.858	80
.933	85		

These runs were made with a 40% slurry, using 3100 grams of Type I Portland cement and 1240 grams of distilled water.

TABLE XX

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 4

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	23,700		4.00	5,925
2	23,800	0.07	3.93	6,056
3	26,600		4.00	6,650
4	24,700	0.03	4.00	6,175
5	25,000		4.00	6,250
6	22,200		4.00	5,550
7	25,200		4.00	6,300
8	25,600		4.00	6,400
9	None	Too faulty to be tested		

Average compressive strength of all values = 6163 psi

Allowable deviation = ± 616 psi

Allowable limits are 5547 - 6779 psi

True average compressive strength = 6163 psi

TABLE XXI

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 5

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	17,200		4.00	4,300
2	18,200		4.00	4,550
3	16,800		4.00	4,200
4	13,500		4.00	3,375
5	17,000		4.00	4,250
6	13,600		4.00	3,400
7	19,000		4.00	4,750
8	16,400		4.00	4,100
9	14,900		4.00	3,725
10	17,300		4.00	4,325
11	18,450		4.00	4,612
12	14,700		4.00	3,675

Average compressive strength of all values = 4036 psi

Allowable deviation = ± 404 psi

Allowable limits are 3632 - 4440 psi

True average compressive strength = 4079 psi

TABLE XXII

SLURRY CONSISTENCIES FOR RUN NO. 6 AT 180°F

RUN NO. 6		
Time From Start Of Run, Hours	Consistency In Poises	
0	25	This run was made with a 40% slurry, using 3100 grams of Type I Portland cement and 1240 grams of distilled water.
.167	27	
.317	29	
.400	37	
.475	42	
.517	47	
.567	67	
.592	77	
.600	83	

TABLE XXIII

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 6

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	17,100	0.12	3.88	4,407
2	16,950	0.06	4.00	4,237
3	16,300	0.25	3.75	4,347
4	18,400		4.00	4,600
5	17,200	0.10	3.90	4,410
6	16,600	0.25	3.75	4,427
7	17,800	0.08	3.92	4,540
8	19,000		4.00	4,750
9	17,950	0.06	4.00	4,487
10	18,700		4.00	4,675
11	18,500	0.08	3.92	4,719
12	18,650		4.00	4,662

Average compressive strength of all values = 4522 psi

Allowable deviation = ± 452 psi

Allowable limits are 4070 - 4974 psi

True average compressive strength = 4522 psi

TABLE XXIV

SLURRY CONSISTENCIES FOR RUN NO. 7 AT 140°F

Time From Start Of Run, Hours	Consistency In Poises	
0	28	This run was made with a 40% slurry, using 3100 grams of Type I Portland cement and 1240 grams of distilled water.
.158	28.5	
.325	32	
.508	36	
.592	43	
.725	47	
.825	57	
.925	64	
.966	77	
.975	81	
.983	86	

TABLE XXV

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 7

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	18,900		4.00	4,725
2	16,800		4.00	4,200
3	16,900		4.00	4,225
4	17,800		4.00	4,450
5	16,000		4.00	4,000
6	16,400	0.06	4.00	4,100

Average compressive strength of all values = 4286 psi

Allowable deviation = ± 429 psi

Allowable limits are 3857 and 4715 psi

True average compressive strength = 4195 psi

CALCULATION OF TRUE AVERAGE COMPRESSIVE STRENGTH FOR ALL CUBES AT 140°F-RUNS NO. 5 AND 7

Overall average compressive strength of all 18 values from Runs No. 5 and 7 = 4167 psi

Allowable deviation = ± 417 psi

Allowable limits are 3750 - 4584 psi

True average compressive strength = 4249 psi

TABLE XXVI

SLURRY CONSISTENCIES FOR RUN NO. 8 AT 140°F

Time From Start Of Run, Hours	Consistency In Poises
0	28
0.117	35
0.250	44
0.333	51
0.367	60
0.400	75
0.425	84
0.458	92

This run was made with a 40% slurry using 3100 grams of Type I Portland cement and 1240 grams of distilled water and 10.6400 grams of $Na_4P_2O_7 \cdot 10\ H_2O$ as an additive.

TABLE XXVII

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 8

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	14,850		4.00	3,712
2	13,100		4.00	3,275
3	15,350		4.00	3,838
4	15,700		4.00	3,925
5	13,950	0.05	4.00	3,487
6	15,300		4.00	3,825

Average compressive strength of all values = 3677 psi

Allowable deviation = ± 368 psi

Allowable limits are 3309 - 4045 psi

True average compressive strength = 3757 psi

TABLE XXVIII

SLURRY CONSISTENCIES FOR RUN NO. 9 AT 140°F

Time From Start Of Run, Hours	Consistency In Poises
0	24
0.05	28
0.167	30
0.367	34
0.500	37
0.675	37
0.833	40
1.116	40
1.300	39
1.466	39
1.700	47
2.100	50
2.567	50
2.950	54
3.433	54
3.766	58
3.942	57
4.025	65
4.366	61
4.767	64
5.041	68
5.341	75
5.483	68.5
5.733	69
6.058	77
6.233	70

This run was made with a 40% slurry using 3100 grams of Type I Portland cement and 1240 grams of distilled water and 6.3450 grams of quebracho as an additive.

TABLES XXIX AND XXX

SLURRY CONSISTENCIES FOR RUNS NO. 10 AND 11 AT 140°F

RUN NO. 10	
Time From Start Of Run, Hours	Consistency In Poises
0	27.5
0.191	28
0.358	28
0.525	30
0.692	32.5
0.858	35
1.033	43
1.192	48
1.442	79
1.475	90

RUN NO. 11	
Time From Start Of Run, Hours	Consistency In Poises
0	26
0.183	30
0.333	32
0.492	34
0.658	35
0.867	36
0.992	36
1.150	36.5
1.325	40
1.442	41
2.008	60
2.108	64
2.167	70
2.225	85

These runs were made with 40% slurries using 3100 grams of Type I Portland cement and 1240 grams of distilled water, each. Run No. 10 used 1.5863 grams of quebracho additive and Run No. 11 used 3.1725 grams of quebracho additive.

TABLE XXXI

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 9

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	18,500	0.09	3.91	4,731
2	21,000	0.08	3.92	5,357
3	19,800	0.06	4.00	4,950
4	22,050	0.06	4.00	5,512
5	26,100	0.25	3.75	6,960
6	22,200	0.30	3.70	6,000

Average compressive strength of all values = 5586 psi

Allowable deviation = ± 559 psi

Allowable limits are 5027 - 6145 psi

True average compressive strength = 5623 psi

TABLE XXXII

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 10

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	20,750	0.04	4.00	5,188
2	16,800		4.00	4,200
3	19,150	0.10	3.90	4,910
4	18,740	0.30	3.70	5,065
5	19,800	0.45	3.55	5,577
6	19,200	0.35	3.65	5,260

Average compressive strength of all values = 5033 psi

Allowable deviation = ± 503 psi

Allowable limits are 4530 - 5536 psi

True average compressive strength = 5106 psi

TABLE XXXIII

SLURRY CONSISTENCIES FOR RUN NO. 12 AT 140°F

Time From Start Of Run, Hours	Consistency In Poises
0	25
0.167	28
0.333	28.5
0.433	29
0.600	35
0.767	36
0.883	37
1.158	38.5
1.517	40
1.967	42
2.333	43
2.575	46
2.867	49
3.308	52
3.650	59
3.892	69
4.267	58
4.350	68
4.400	85

This run was made with a 40% slurry using 3100 grams of Type I Portland cement and 1240 grams of distilled water and 4.7588 grams of quebracho as an additive.

TABLE XXXIV

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 11

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	17,400		4.00	4,350
2	21,900		4.00	5,475
3	18,300		4.00	4,575
4	21,500		4.00	5,375
5	19,750		4.00	4,937
6	19,600		4.00	4,900

Average compressive strength of all values = 4935 psi

Allowable deviation = ± 494 psi

Allowable limits are 4441 - 5429 psi

True average compressive strength = 4947 psi

TABLE XXXV

COMPRESSIVE STRENGTHS OF CEMENT FROM RUN NO. 12

Cube No.	Total Strength In Lbs.	Faulty Area In Sq. In.	Compressive Area In Sq. Inches	Compressive Strength In Psi
1	23,800	0.05	4.00	5,950
2	24,600	0.05	4.00	6,150
3	24,250	0.08	3.92	6,186
4	26,100		4.00	6,525
5	24,450	0.05	4.00	6,112
6	24,000	0.25	3.75	6,400

Average Compressive strength of all values = 6221 psi

Allowable deviation = ± 622 psi

Allowable limits are 5599 - 6843 psi

True average compressive strength = 6221 psi

APPENDIX C

GRAPHS OF EXPERIMENTAL DATA

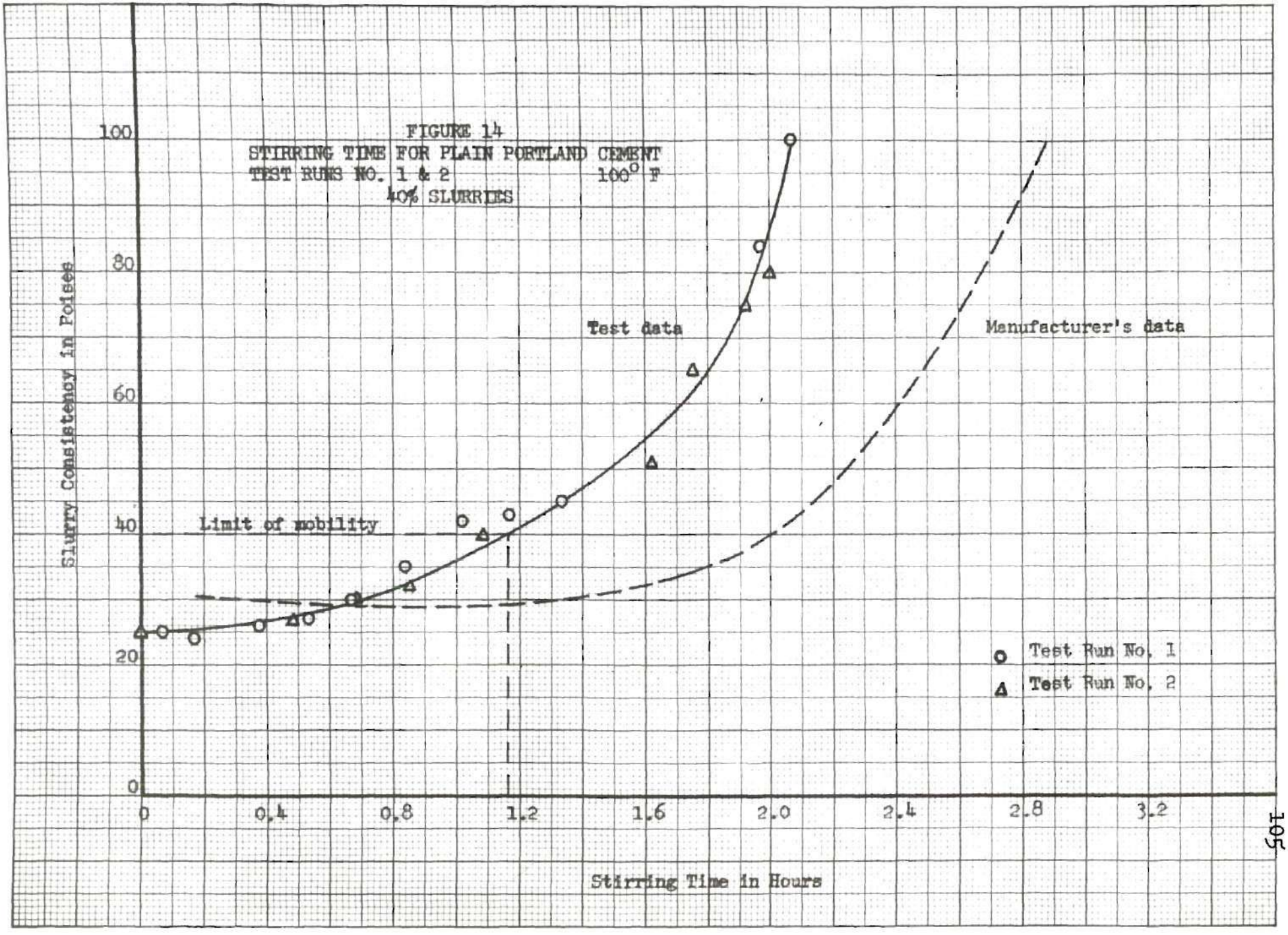


FIGURE 14
STIRRING TIME FOR PLAIN PORTLAND CEMENT
TEST RUNS NO. 1 & 2 100° F
40% SLURRIES
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
Test data
Manufacturer's data
Test Run No. 1
Test Run No. 2
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
Stirring Time in Hours

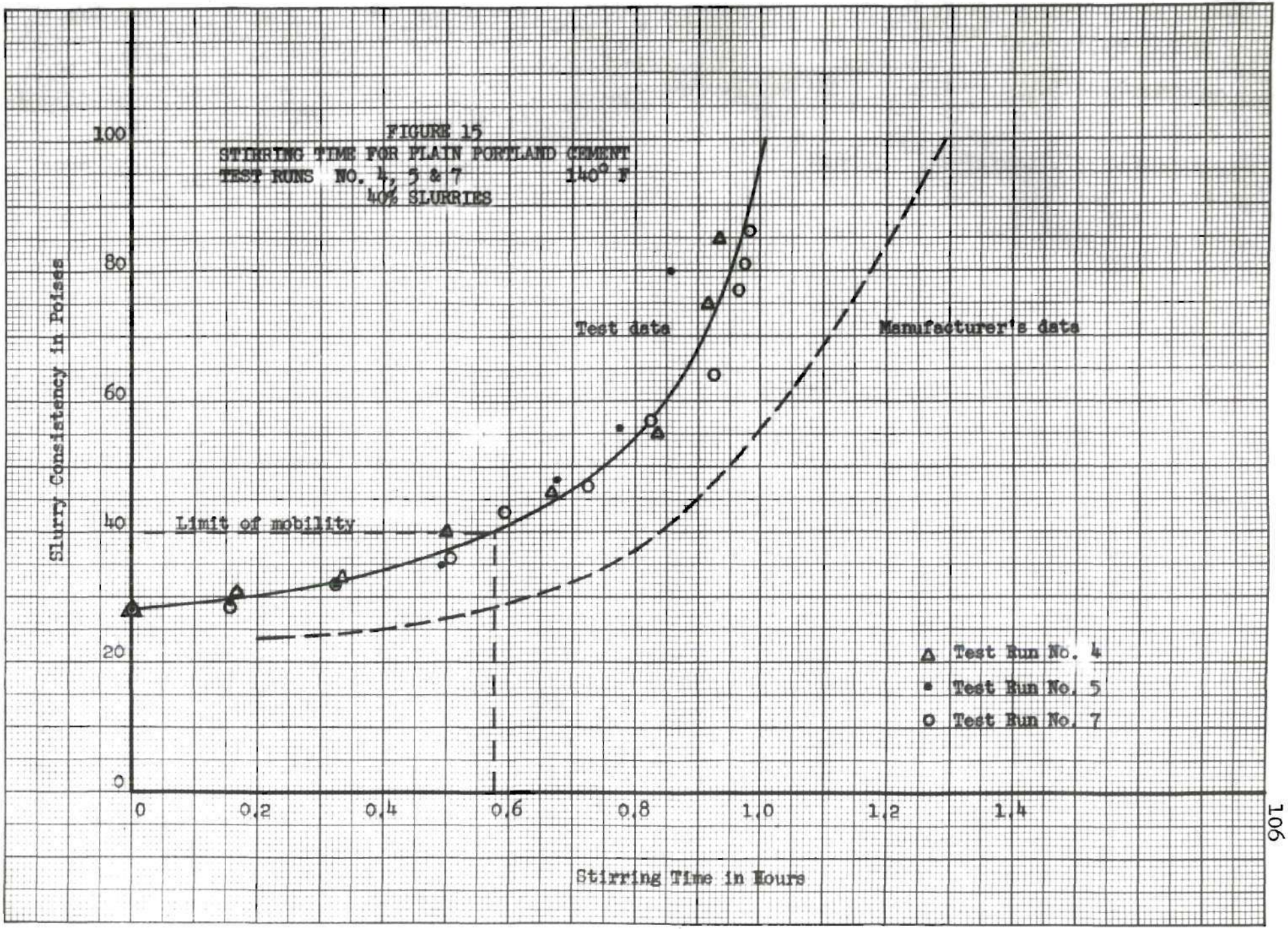


FIGURE 15
STIRRING TIME FOR PLAIN PORTLAND CEMENT
TEST RUNS NO. 4, 5 & 7 140° F
40% SLURRIES
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
Test data
Manufacturer's data
Δ Test Run No. 4
• Test Run No. 5
o Test Run No. 7
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Stirring Time in Hours

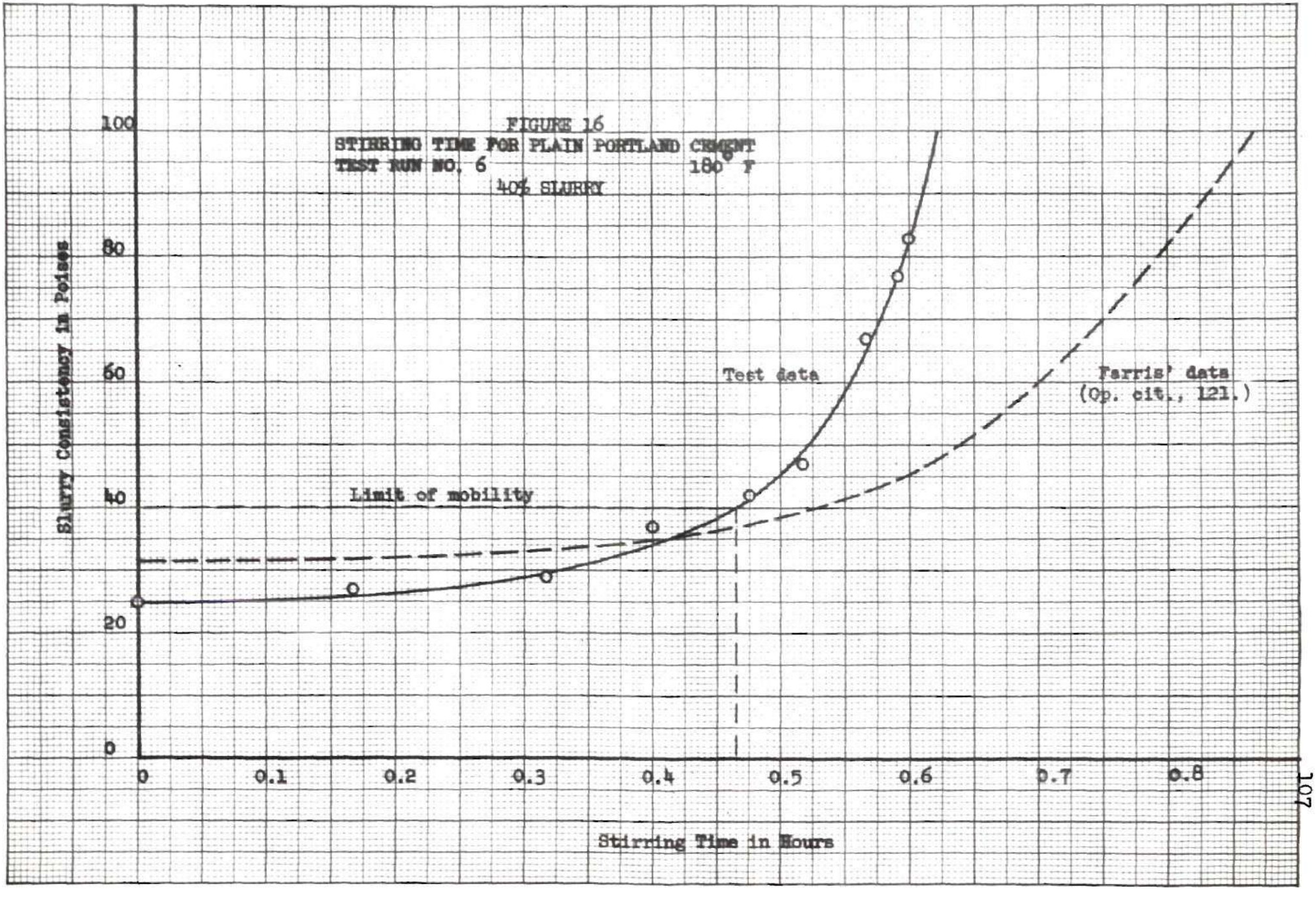


FIGURE 16
STIRRING TIME FOR PLAIN PORTLAND CEMENT
TEST RUN NO. 6
180° F
40% SLURRY
Slurry Consistency in Poises
100
80
60
40
20
0
Test data
Farris' data
(Op. cit., 121.)
Limit of mobility
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Stirring Time in Hours

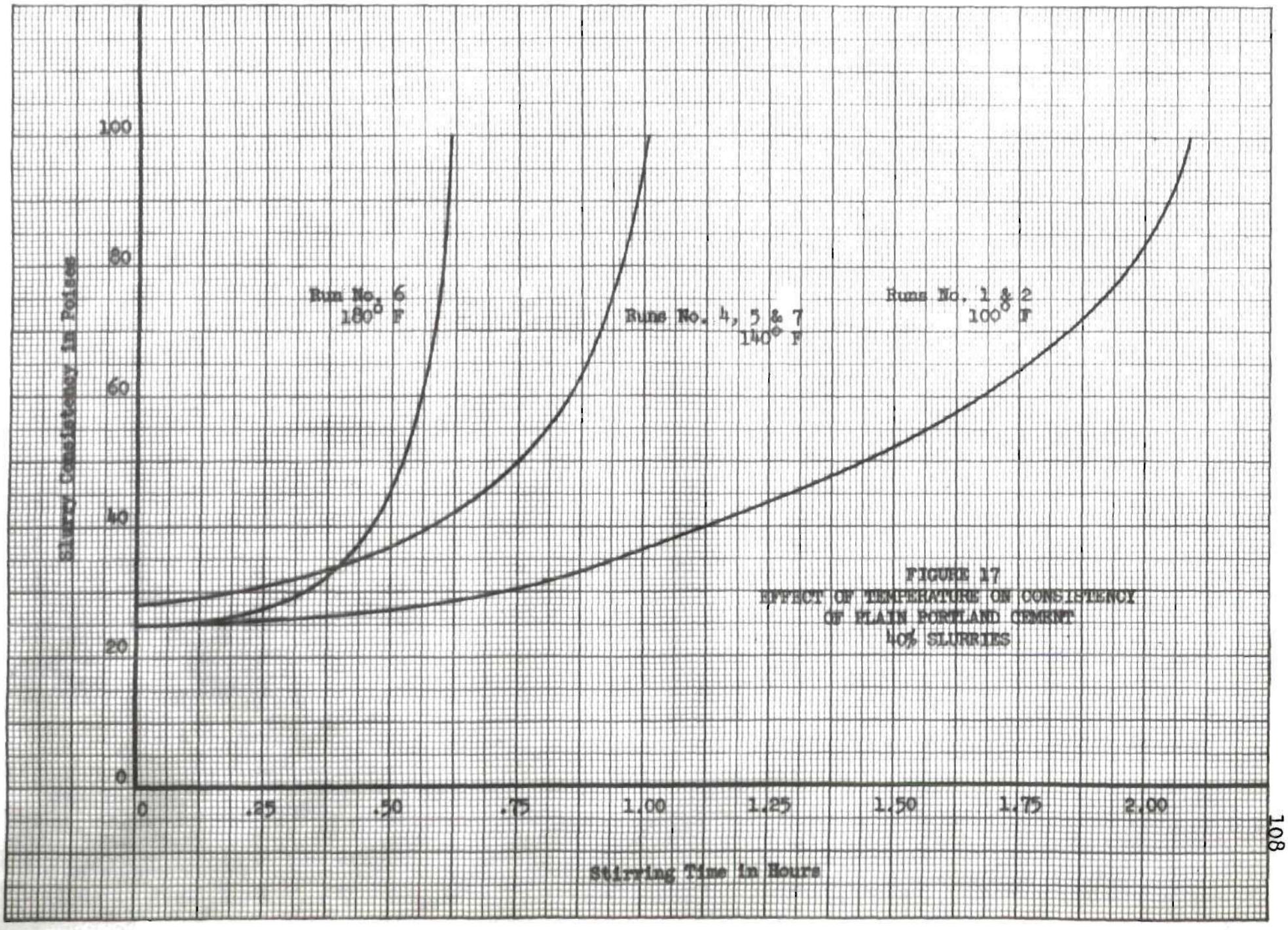


FIGURE 17
EFFECT OF TEMPERATURE ON CONSISTENCY
OF PLAIN PORTLAND CEMENT
40% SLURRIES

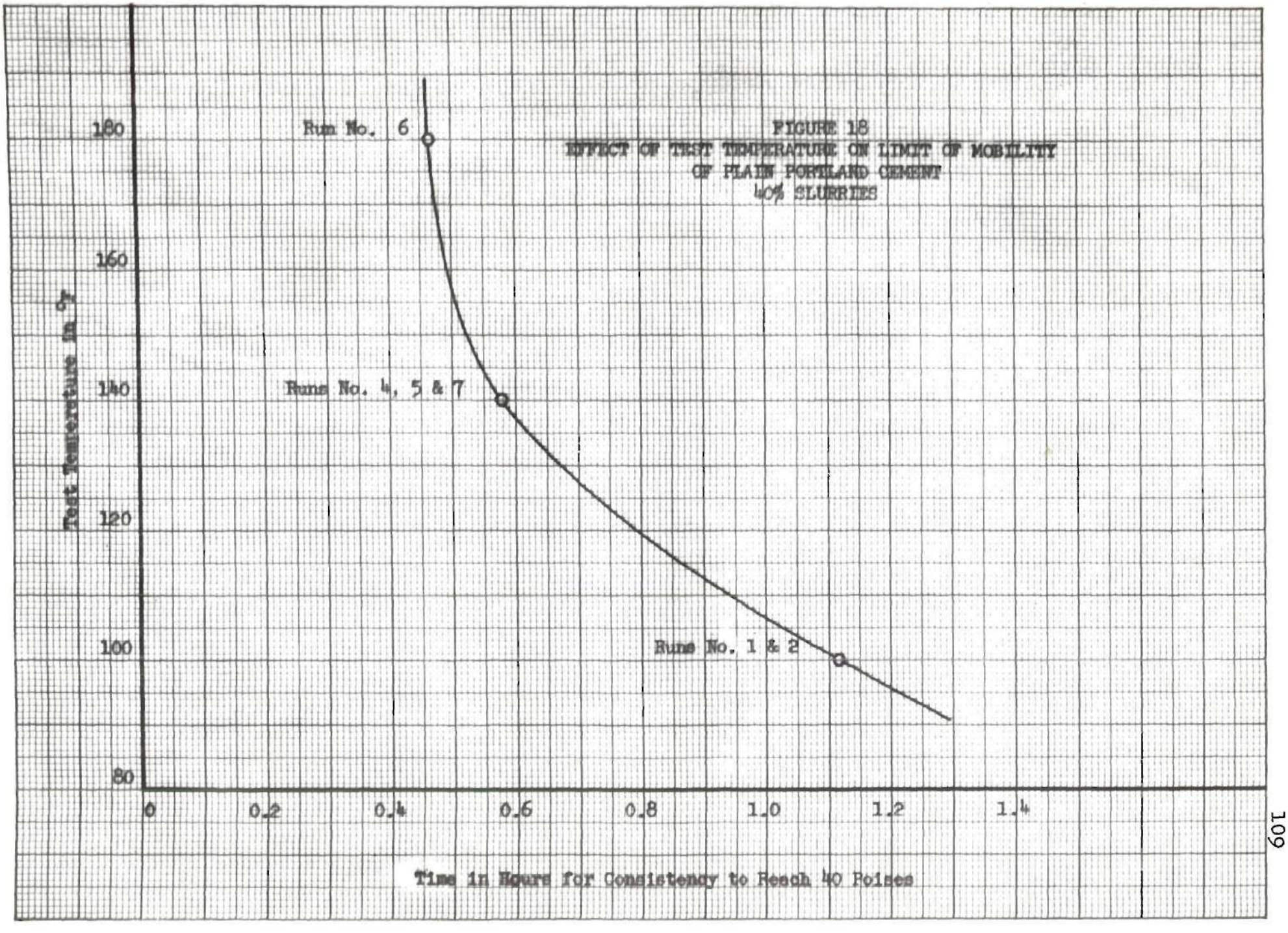


FIGURE 18
EFFECT OF TEST TEMPERATURE ON LIMIT OF MOBILITY
OF PLAIN PORTLAND CEMENT
40% SLURRIES

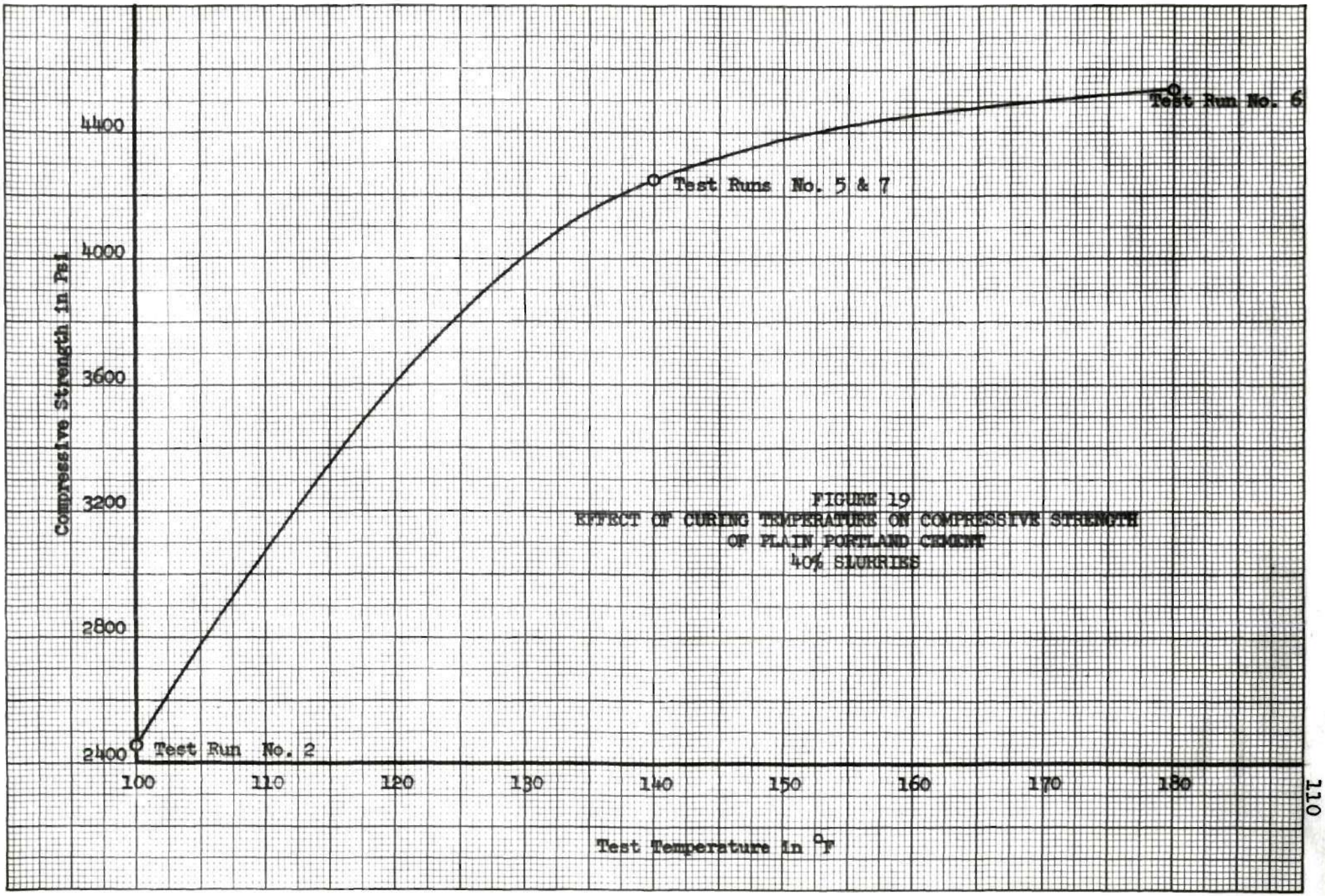


FIGURE 19
EFFECT OF CURING TEMPERATURE ON COMPRESSIVE STRENGTH
OF PLAIN PORTLAND CEMENT
40% SLURRIES

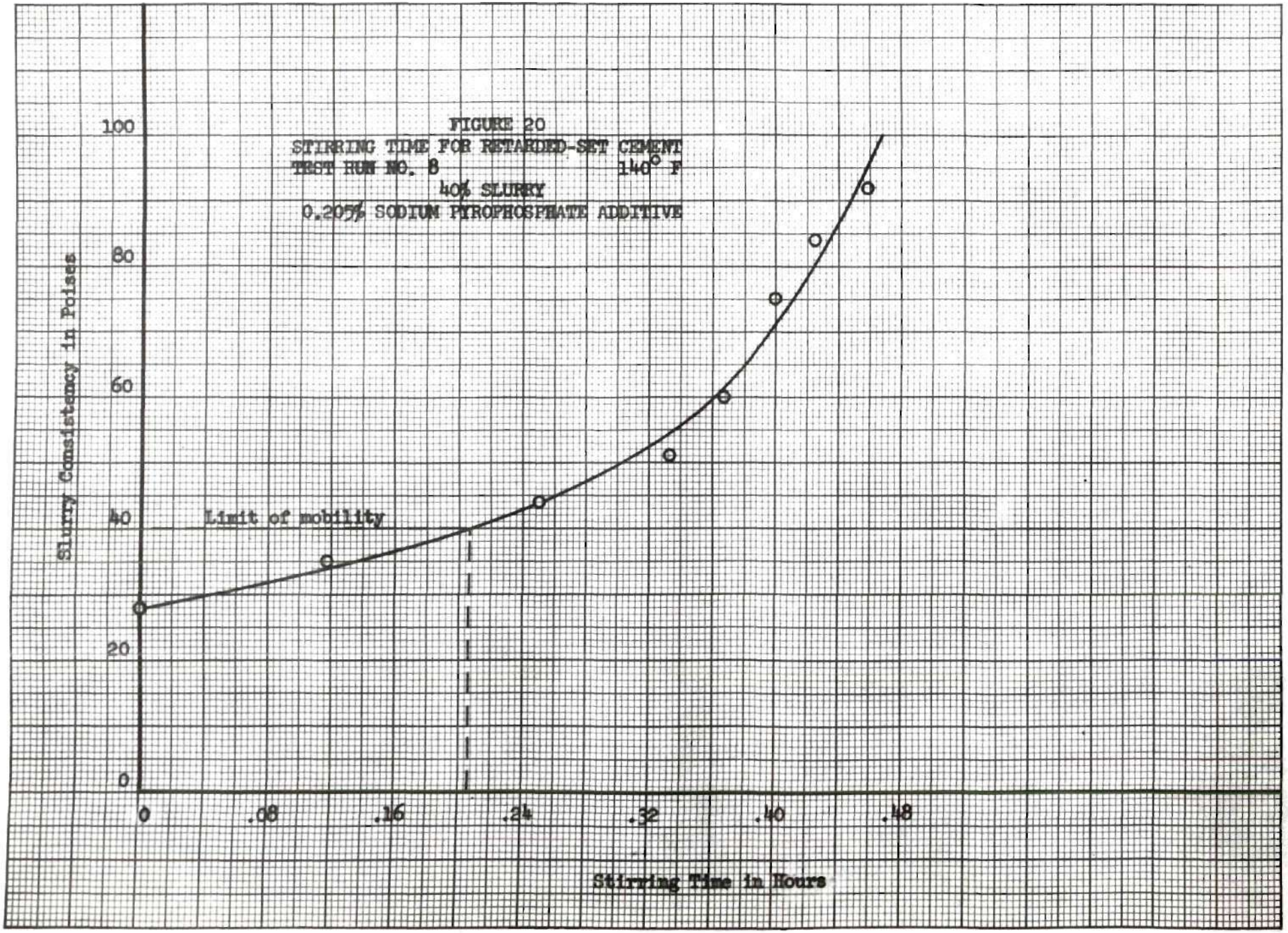


FIGURE 20
STIRRING TIME FOR RETARDED-SET CEMENT
TEST RUN NO. 8 140° F
40% SLURRY
0.205% SODIUM PYROPHOSPHATE ADDITIVE
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
0
.08
.16
.24
.32
.40
.48
Stirring Time in Hours

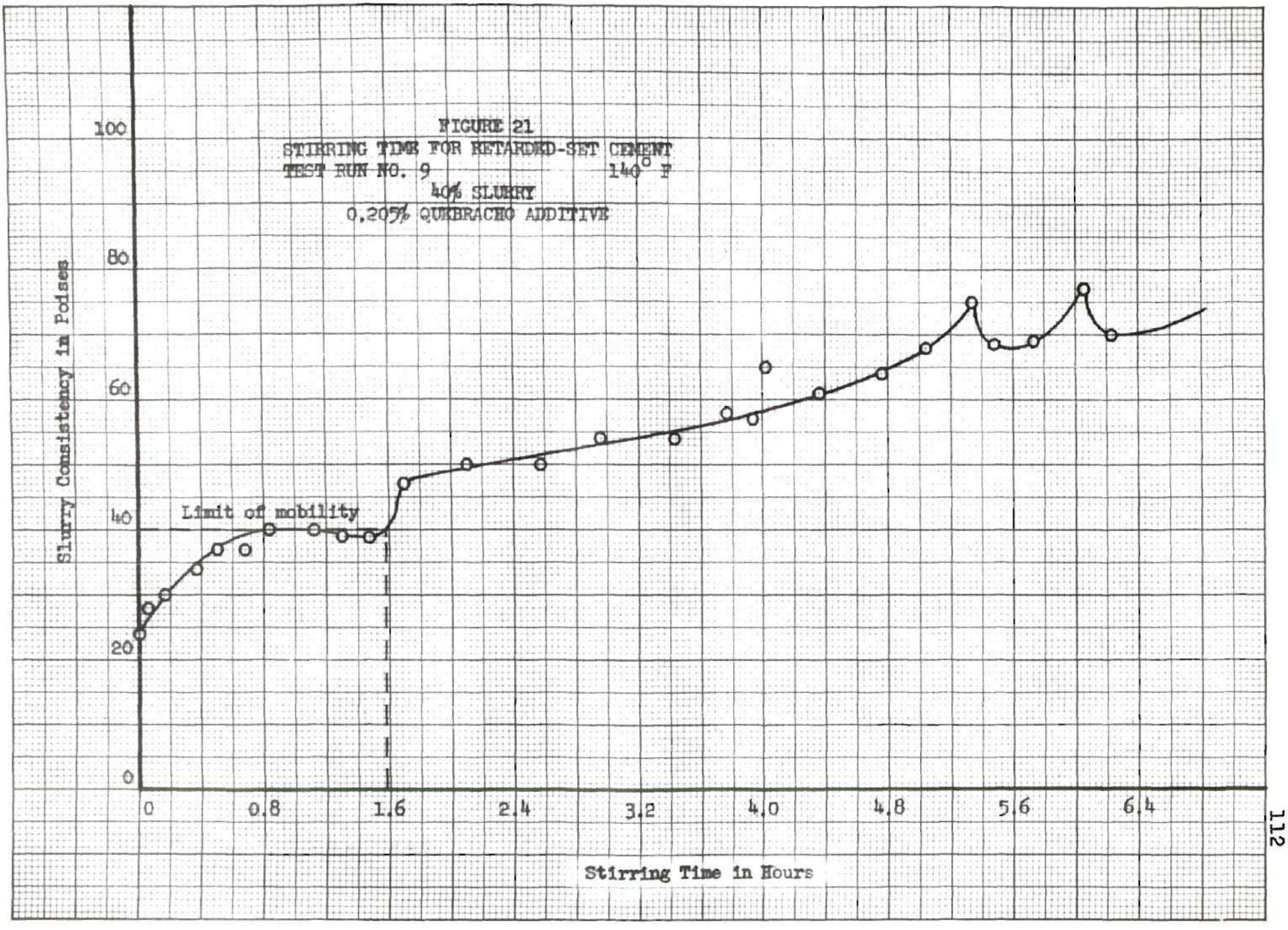
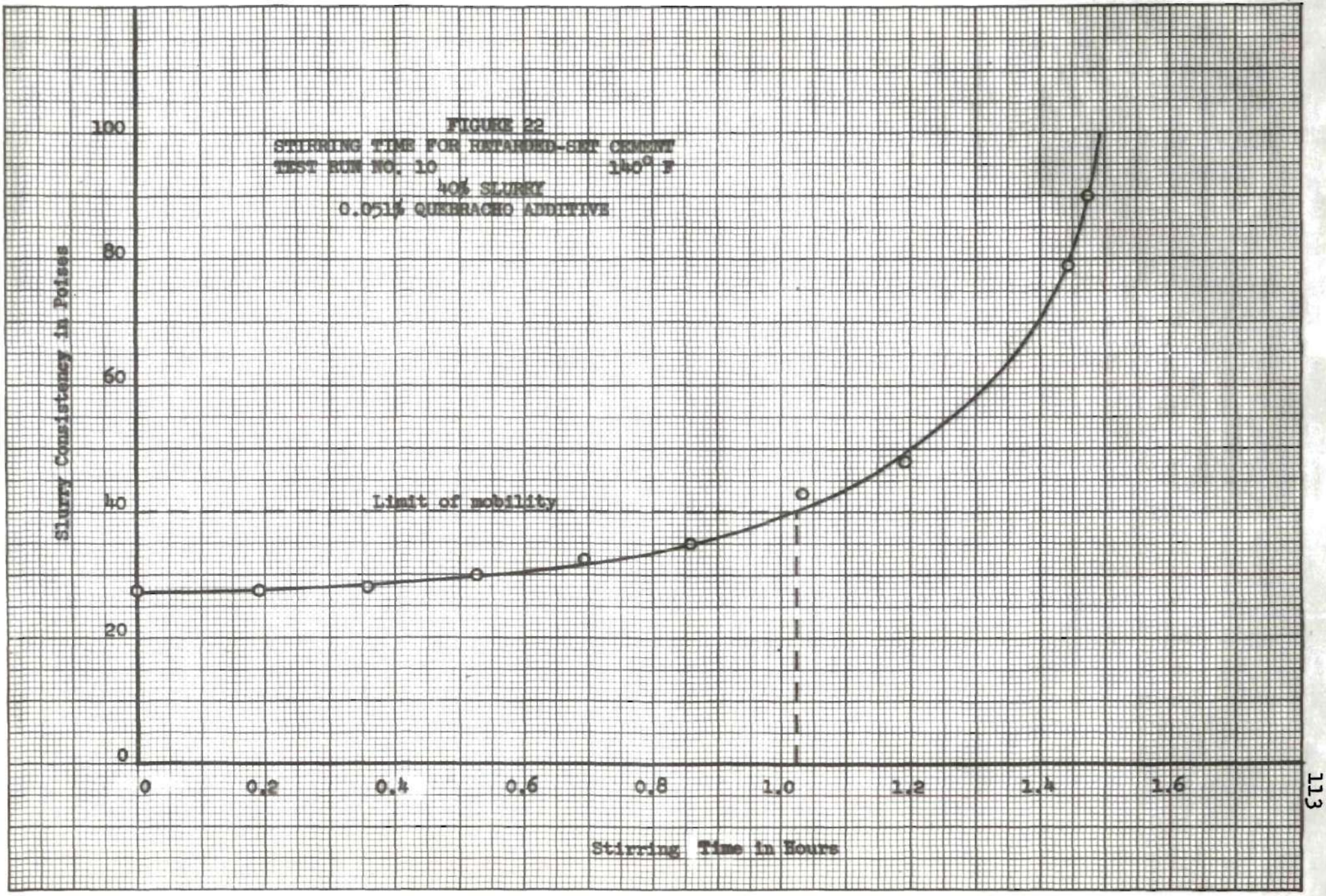


FIGURE 21
STIRRING TIME FOR RETARDED-SET CEMENT
TEST RUN NO. 9 140° F
40% SLURRY
0.20% QUEBRACHO ADDITIVE
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
0
0.8
1.6
2.4
3.2
4.0
4.8
5.6
6.4
Stirring Time in Hours

FIGURE 22
STIRRING TIME FOR RETARDED-SET CEMENT
TEST RUN NO. 10 140° F
40% SLURRY
0.051% QUEBRACHO ADDITIVE



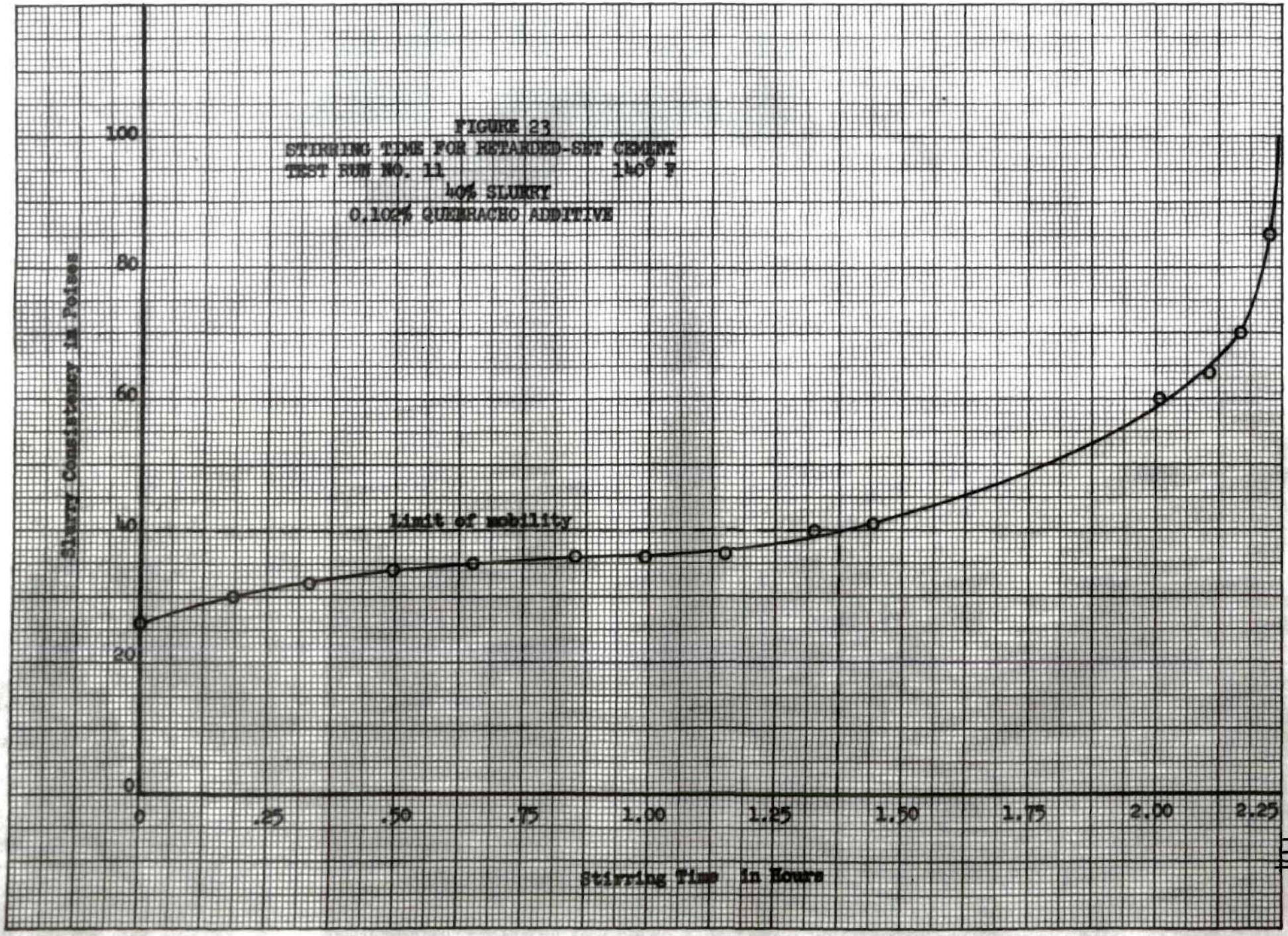


FIGURE 23
STIRRING TIME FOR RETARDED-SET CEMENT
TEST RUN NO. 11 140° F
40% SLURRY
0.102% QUEBRACHO ADDITIVE
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
0
.25
.50
.75
1.00
1.25
1.50
1.75
2.00
2.25
Stirring Time in Hours

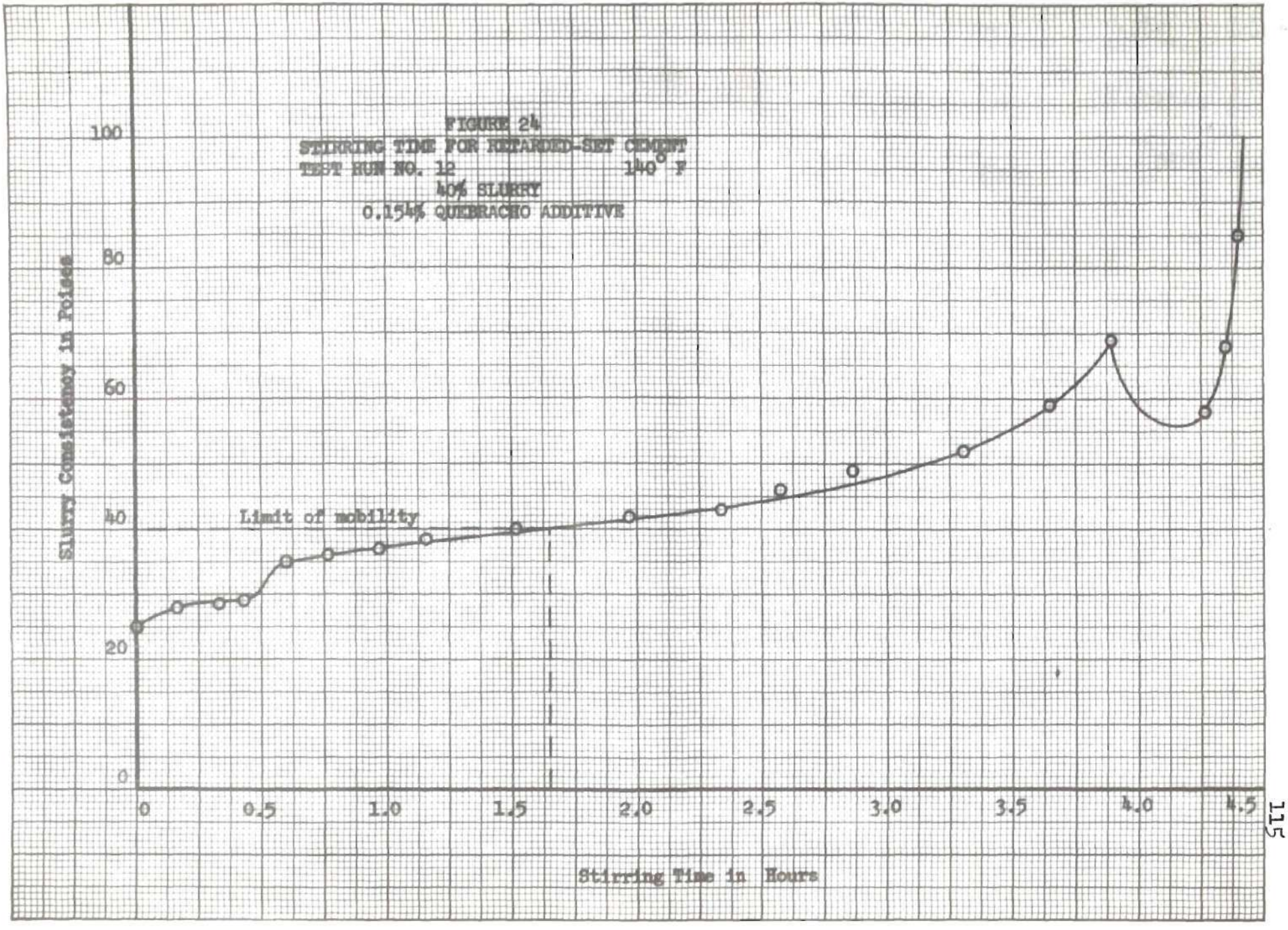
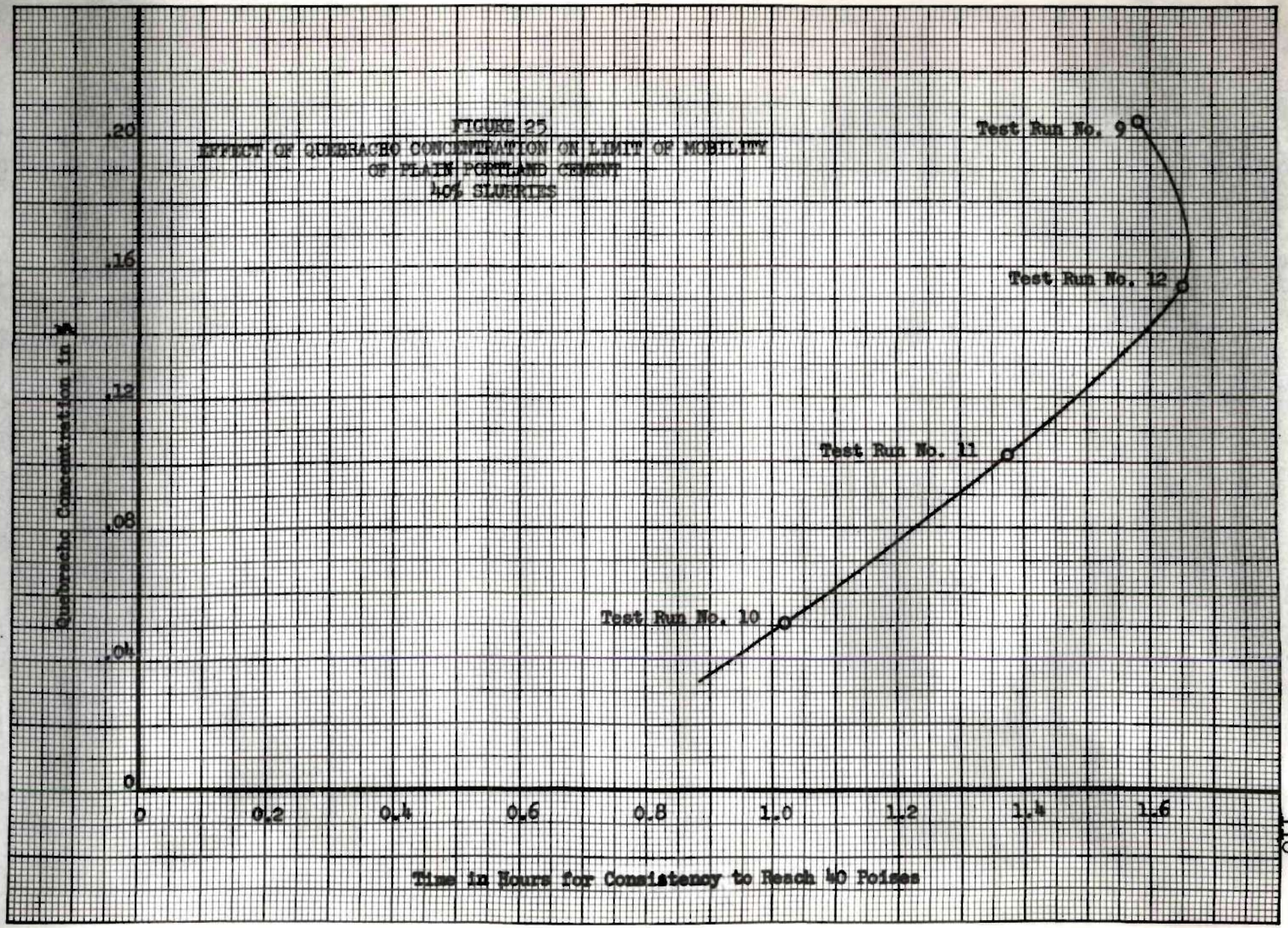


FIGURE 24
STIRRING TIME FOR RETARDED-SET CEMENT
TEST RUN NO. 12 140° F
40% SLURRY
0.15% QUEBRACHO ADDITIVE
Slurry Consistency in Poises
100
80
60
40
20
0
Limit of mobility
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Stirring Time in Hours

FIGURE 25

EFFECT OF QUEBRACHO CONCENTRATION ON LIMIT OF MOBILITY OF PLAIN PORTLAND CEMENT 40% SLURRIES



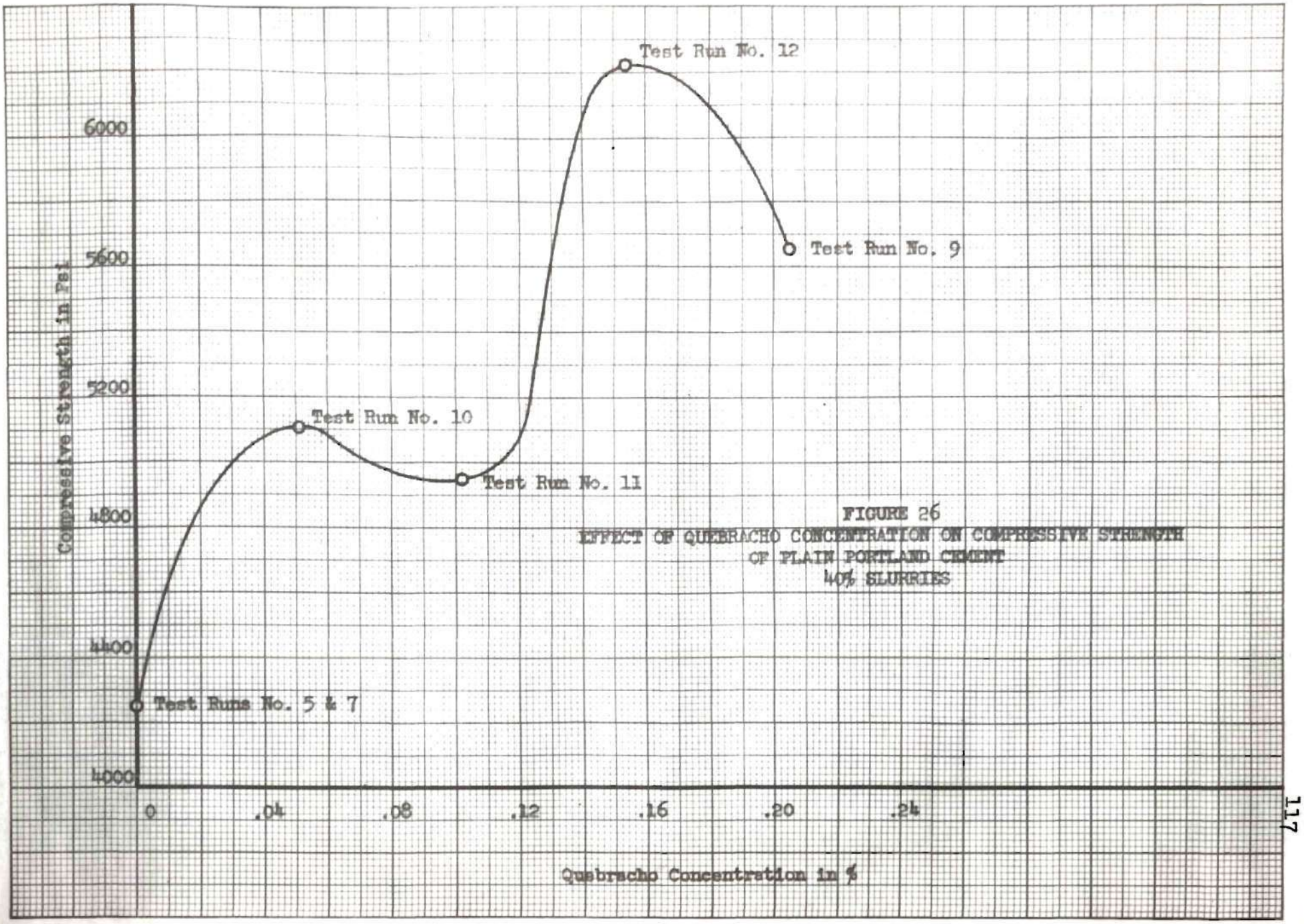


FIGURE 26
EFFECT OF QUEBRACHO CONCENTRATION ON COMPRESSIVE STRENGTH
OF PLAIN PORTLAND CEMENT
40% SLURRIES

APPENDIX D

SAMPLE CALCULATIONS

(1) Amount of chemical additive used, grams, lbs./bbl. slurry, and % by weight of dry cement.

The calculations were first made on the basis of the equivalent pounds that would be added per barrel of slurry in actual field operations. The concentrations in terms of percentage and actual amount to be added in grams were converted from these values, as follows:

Basis: 1.0 lbs./bbl. slurry -- using 40% slurry,

where % is (gms. water/gm. cement) X 100

Density of 40% slurry is 16.3 lbs./gal.

1 bbl. is 42 gals., so 1 bbl. slurry has the total weight: (42) X (16.3) = 684.6 lbs.

Then, reagents will be added at the rate of 1.0 lb./684.6 lbs. slurry, to achieve an additive composition of 1.0 lb./bbl.

Also, 1.0/684.6 = 0.001462 grams additive/gm. slurry. Since it was found by experimentation that approximately 4300 grams of slurry are required to fill the consistometer can, the following batch size requirements were specified:

3100 grams of dry cement

3100 X (0.40) = 1240 grams of mixing water.

Total weight of slurry = (3100 + 1240) = 4340 grams. The amount of reagent to be used is then calculated:

Grams additive = (4340) X (0.001462) = 6.345 grams. Since it is thought that the amount of retardant used should be based on the reactive portion it actually contributes to the slurry, a correction was made for the water of hydration that is included in the sodium pyrophosphate molecule as the decahydrate, $Na_4P_2O_7 \cdot 10H_2O$.

Molecular weight of the decahydrate is 446.11

Reactive molecular weight = (M. W.) - $10(H_2O)$

= 446.11 - (10) X (18.02) = 265.91.

Therefore, a conversion factor is postulated, thusly:

$$\text{Reactive fraction} = \frac{265.91}{446.11} = 0.59606$$

The amount of decahydrate to be added to achieve a concentration of 1.0 lb. reactive material/bbl. slurry is:

6.345/0.59606 = 10.644 lbs.

This is equivalent to 10.644 grams/4340 grams slurry.

Using quebracho for various fractional concentrations such as 0.75, 0.50 and 0.25 lbs./bbl., the value of 6.345 is multiplied by the fractional concentration to calculate the amount required. That is:

Amount of quebracho for a slurry additive concentration of 0.25 lbs./bbl. of slurry

= (0.25) X (6.345) = 1.5862 grams.

The percentage concentration of the additive in the slurry is calculated in this manner:

% additive = (grams additive/grams dry cement) X 100

For a specific case, corresponding to a field concentration of 1.0 lbs./bbl. of slurry, this is:

% additive = (6.345/3100) X 100 = 0.205% quebracho

(2) Compressive strength of hardened cement, psi.

The compressive strength of a cube was to be calculated on the actual area of the least-sized bearing face, if the cube were faulty, more than 0.06 sq. in. On the other hand, if the missing area were 0.06 sq. in. or less, the values were to be calculated on the basis of an area of 4.00 sq. in. These calculations are illustrated as follows:

Run No. 12 - Cube No. 3

Missing area is 0.08 sq. in.

Compressive strength = 24,250/(4.00 - 0.08)

= 6,186 psi.

Run No. 6 - Cube No. 9

Missing area is 0.06 sq. in.

Compressive strength = 17,950/(4.00)

= 4,487 psi.

In order to calculate the average compressive strength of all the cubes from any one run, or groups of runs at the

same temperature, in the case of plain Portland cement, the ASTM standard specifies[36] that cubes which are obviously faulty, or give compressive strength values deviating more than ± 10 % from the average value for all the cubes tested, will not be considered in calculation of the true average value. Such a condition may be illustrated by the data from Run No. 10.

Average value of compressive strength for all cubes

$$= \frac{5188 + 4200 + 4910 + 5065 + 5577 + 5260}{6} = 5033 \text{ psi.}$$

Allowable deviation = ± 503 psi, thus the limits of acceptibility are 4530 and 5536 psi.

Of all the original values, only cubes no. 1, 3, 4 and 6 are within the limits. The true average compressive strength for the run is calculated by averaging these four values.

True average compressive strength for Run No. 10

$$= \frac{5188 + 4910 + 5065 + 5260}{4} = 5106 \text{ psi.}$$

This latter procedure was followed in calculating the true average compressive strength for the total of more than one run at the same temperature, for example, Runs No. 5 and 7. In such a case, all the test values were first averaged together to find the compressive strength, without regard to the run number. Then the allowable deviations and limits were calculated and applied to all the values,

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[36] Am. Soc. Testing Materials, Standards. Part II, 81, (1944).

in order to select only the ones which would apply to the true average compressive strength for both runs. In every case, only these true average values were used for plotting results of compressive strength tests.